CHEMICAL ENGINEERING SCIENCE
GENIE CHIMIQUE

VOL. 4 AUGUST 1955 No. 4

Some factors affecting droplet behaviour in liquid-liquid systems

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(*Received* 18 *February*, 1955)

Abstract—In an earlier paper [8] it was shown by visual observation of colour-change reactions that circulation currents within a droplet were caused by the frictional drag of the outer fluid, but only above a certain transition Reynolds number. The presence of circulation currents inside a droplet greatly accelerates mass transfer; thus, for the aqueous extraction of acetic acid from nitrobenzene droplets, a 2·5 to 4·5 fold increase resulted over that expected from stagnant drops [9].

Observation of colour-change reaction and of flow patterns revealed by aluminium particles has now shown that, for droplets moving in water, a vortex becomes established in the wake of the drop above a Reynolds number of about 20, while the Reynolds number, at which circulation begins within a drop, decreases with increasing viscosity of the outer phase. Evidence is given supporting the earlier conclusion that droplets circulate less readily the higher the interfacial tension of the system.

Trace quantities of impurities which are surface active in character may inhibit internal circulation, but this effect can be partially overcome by the presence of a diffusing solute readily miscible in both phases.

As compared with rigid spheres of the same size and density, internal circulation may substantially increase droplet fall velocities (an increase of about 50% was observed for one system) while oscillation of a prolate – oblate type will reduce the fall velocity – a reduction of at least 12% being obtained in one case.

Résumé—Dans un article précédent, les auteurs ont montré par l'observation visuelle les changements de teintes que les courants de circulation à l'intérieur d'une gouttelette sont dûs à la résistance de friction du liquide extérieur, mais seulement au-dessus d'un certain nombre de Reynolds de transition. La présence de ces courants internes accélère le transfert de masse : Par exemple, pour l'extraction de l'acide acétique par des gouttelettes de nitrobenzène, l'augmentation est de 2,5 à 4,5 fois celle que l'on attendrait de gouttes rigides. L'observation des changements de teinte et des trajectoires à l'aide de particules d'aluminium a montré qu'au-dessus d'un nombre de Reynolds d'environ 20, et pour des gouttelettes tombant dans l'eau, il s'établit un vortex dans le sillage de la goutte, tandis que le nombre de Reynolds pour lequel la circulation commence à l'intérieur d'une goutte décroît avec l'augmentation de viscosité de la phase extérieure.

Il se confirme que les gouttes circulent d'autant moins facilement que la tension interfaciale du système est élevée.

Les traces d'impuretés, de caractère tensio-actif, annulent la circulation interne, mais cet effet peut être partiellement surmonté par la diffusion d'un soluté rapidement miscible dans les deux phases. Par comparaison avec des sphères rigides de mêmes dimensions et densités, la circulation interne peut accroître de façon substantielle la vitesse de la goutte (environ 50% dans un des cas) tandis qu'un mouvement oscillatoire d'allongement et d'aplatissement de la goutte réduira la vitesse de chute (environ 12% dans un cas).

The Transition from Streamline to Eddying Flow around Liquid Droplets in Water

When a sphere moves very slowly through a fluid, the flow pattern within that fluid is completely streamline, and the pattern in the wake is the same as that in front of the sphere. With increasing speed, however, a transition velocity is reached above which an eddy or vortex ring appears behind the sphere. Johnstone and Williams [13] consider that the vortex becomes "unstable" at Reynolds numbers around 150, but this has not been confirmed by R. W. Grafton who worked in this field in this department. Nisi and Porter [15] experimented with solid spheres in air and found that eddies first formed behind the sphere at a Reynolds number of 8·15. Using solid spheres in water, Möller [14] reported eddies forming at a Reynolds number of 300, though the experiments of Williams [18] on solid spheres in glycerine failed to show production of such eddies up to Reynolds numbers of 720. On the other hand, Bond [4] states that the transition Reynolds number for a sphere is "of the order of unity."

We observed the transition point, using ethanolamine as diffusing solute passing from the drops into water containing about 10 cc of standard phenolphthalein solution per litre. The red coloration produced by diffusion of the amine revealed the presence or absence of eddies behind the droplets. Observation was greatly facilitated by viewing against an illuminated background which was half black and half white, the droplet being viewed along the vertical boundary line between black and white, though near the transition region the eddies were feeble and poorly defined.

Two mixtures of different density and solute concentrations were used (see following Table for composition), and for each droplet the fall velocity was recorded together with a comment on the presence or absence of eddies observed in its wake. Fall velocities were measured by stop watch and used to obtain Reynolds numbers (*Re*) from a plot of C_D/Re vs. *Re*, where C_D is drag coefficient. The method, which uses experimental data relating to solid spheres, was described in an earlier paper [8], and whilst it is not valid for drops at higher Reynolds numbers, it is applicable here in view of the low Reynolds number range and the near-stagnancy of the drops.

Mixture 1		*Mixture* 2	
Density at 18°C = 1·009 *gm/cc*		*Density at* 18°C = 1·021 *gm/cc*	
Chloroform	14·4% (vol)	Chloroform	25·2% (vol)
ethanolamine	42·8%	ethanolamine	12·0%
amyl alcohol	42·8%	octyl alcohol	62·8%

Mixture 1 contained a relatively high proportion of water-soluble material, ethanolamine being infinitely soluble and amyl alcohol 2·26% soluble in water. Mixture 2 contained only 12% of water soluble material. The drops of varying sizes were formed from an open tube and fell down a glass column 5 cm in diameter and 70 cm in length.

The temperature of the water used was 10°C, its density taken as 1 gm/cc and viscosity 0·013 poises.

The droplets with the highest velocity in the region of no eddies, and with the lowest velocity in the eddy region, corresponded to Reynolds numbers (*Re*) on either side of the transition point. ($Re = dv\rho/\mu$, where d = drop diameter, v = fall velocity, ρ and μ are density and viscosity of outer phase.)

For droplets of mixture 1, the transition occurred between *Re* of 18·6 and 22·1, and for droplets of mixture 2 between *Re* of 20·9 and 23. Thus it appears that, for two liquids with a large difference in solute concentration, the transition from streamline to eddying flow occurs between Reynolds numbers of 19 and 23, using water as continuous phase.

Effects of Continuous Phase Viscosity on Transition from Stagnancy to Circulation within Droplets

Our earlier work [8] on colour change with droplets containing cobalt chloride and using water

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Table 1.

	(1) ← DROP MIXTURES →		
		↓	
nC_4H_9OH	40% (vol)	(2)	(3)
$CHCl_3$	27%	As for mixture (1)	As for mixture (2)
C_6H_6	33%	plus extra nC_4H_9OH	plus extra nC_4H_9OH
C_9Cl_2	3 gm/100 cc		
+ little nC_4H_9OH + $CHBr_3$			

Drop mixture used	*Continuous phase wt.% cellofas B in water*	*Viscosity of continuous phase centistokes 20°C*	*Specific gravity of continuous phase 20°C*	*Interfacial tension 16°C dynes/cm*	*Specific gravity of disperse phase 18·5°C*	*Viscosity of disperse phase centistokes 20°C*	*Transition velocity of droplet cm/sec*	*Transition Reynolds number Re_T*
(3)	0·00	1·00	1·0	1·04	1·045	1·04	1·61–1·7	64·5–71·5
(2)	0·25	3·80	1·0	1·46	1·02	1·46	1·89–2·122	19·28–23·7
(1)	0·50	11·97	1·0	6·24	1·108	1·24	1·77–1·89	3·2 – 3·59
(1)	0·75	24·22	1·0	6·24	1·108	1·24	1·29–1·42	1·32– 1·5
(1)	1·00	35·60	1·006	6·24	1·108	1·24	1·06–1·13	0·83– 0·91

NOTE.—Interfacial tension of mixture (1) against distilled water was 6·12 dynes/cm

as continuous phase showed transition Reynolds numbers (Re_T) for internal circulation ranging from 60 to 245. BOND and NEWTON [5], on the other hand, in 1928, carried out experiments on velocities of rise and fall of droplets of mercury and water in media such as waterglass, syrup and castor oil, and inferred that the transition occurred at $Re < 1$. SPELLS [17] did work on drops of glycerine and glycerine + water in a fairly viscous outer phase (white oils) and observed internal circulation at $Re < 1$. Viscosities of the water-glass and syrup used by BOND and NEWTON ranged from 200-2,000 poise, and their castor oil had a viscosity of about 20 poise. It was therefore decided to vary the viscosity of the continuous phase while attempting to keep other factors, such as densities of inner and outer phases, droplet viscosity and interfacial tension, constant.

The continuous phase comprised *Cellofas B* (a hydroxylated cellulose) dissolved in distilled water. The solution was centrifuged to remove a number of tiny hair-like fibres, and was then diluted to give solutions containing 0·25, 0·5, 0·75 and 1% *Cellofas B* by weight. Measurements showed that *Cellofas B* was not appreciably surface active and viscosities are given in Table 1.

Droplets were formed from a mixture of 40% n butyl alcohol, 27% chloroform, 33% benzene by volume. 3 gm of cobalt chloride per 100 cc of solution were added to give a deep blue liquid. More C_4H_9OH and a little bromoform were added to alter the rate of fall until smaller droplets were stagnant, while larger ones circulated when falling through the 1% *Cellofas* solution. This mixture was used unaltered for the 0·5, 0·75 and 1% *Cellofas* solutions, but more C_4H_9OH had to be added for the 0·25% *Cellofas* solution, to bring the drop mixture into the transition region. Water diffusing into the drops gave a blue to pink colour change, enabling internal motion to be observed. The drops were formed from an open tube and fell down a 60 cm column of about 5 cm internal diameter.

A peculiar phenomenon was observed in which drops showed initial internal circulation which

was gradually damped out, motion ceasing first in the rear portion of the drop, stagnancy gradually spreading through to the leading pole. This pattern was visually confirmed by the insertion of aluminium powder in the drops. Droplets absorbed no *Cellofas*, since their viscosities were unchanged after passage through the column, and experiments, described later, indicated that the explanation is some form of interfacial contamination by small quantities of surface-active impurity collected during passage of the drop down the column.

Accordingly, observation during the first 25 cm of fall of the occurrence of complete stagnancy or continual circulation was used to determine the transition Reynolds number from fall velocities.

Interfacial tensions were measured by the drop weight method, using a thin walled glass nozzle of I.D. = 0·448 cm (the drop liquor wetted the nozzle to its inner diameter), and values were calculated using the correction factors and method of HARKINS and BROWN [11]. Experimental data appear in Table 1.

The Reynolds number at transition from stagnancy to circulation within the droplets, is plotted against viscosity of the continuous phase in Fig. 1.

The curve appears to be a rectangular hyperbola although it should be noted that the abscissa (viscosity) appears also in the denominator of the ordinate. Nevertheless, it might be expected to be asymtotic to the rectangular axes, since for zero outer phase viscosity the transition Reynolds number should be ∞, while increasing the outer phase viscosity means that the frictional drag increases for a given velocity (in Stokesian region $F = 3\pi\, dv\mu_0$) and hence Re_T will fall.

Confirmation of the hyperbolic nature of the curve is found in Fig. 2, where the log transition Reynolds number is plotted against the log continuous phase viscosity. Differences in droplet viscosity and interfacial tension probably cause the values for the two lowest outer phase viscosities to lie slightly off the line, which gives the following approximate relationship between transition Reynolds number (Re_T) and continuous phase viscosity in centistokes (μ_0)

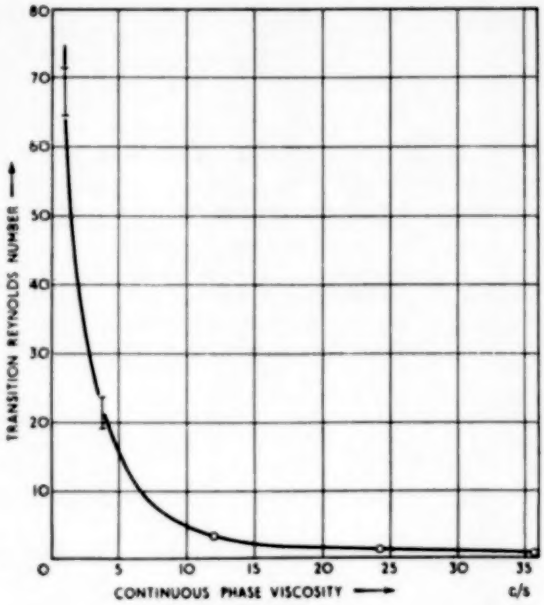

FIG. 1

$$Re_T = 100\,\mu^{-4/3}$$

This applies for droplet viscosities of about 1 to 1·5 c.s. and interfacial tensions of about 1 to 8 dynes/cm.

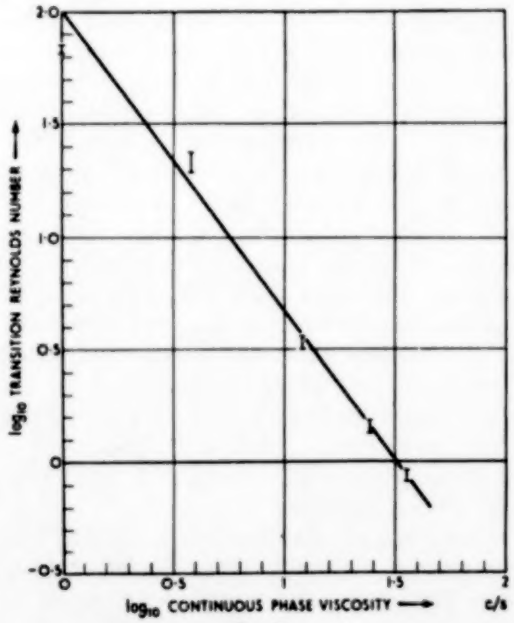

FIG. 2

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Effects of Interfacial Tension on Circulation within Droplets

Experiments showed that the effects of interfacial tension could best be detected at low fall velocities. Redistilled liquids with a wide range of interfacial tensions but with densities near that of the continuous phase (distilled water) were used.

The all-glass apparatus was chemically cleaned, and consisted of a column 95 cm long and 4·5 cm in internal diameter. All drops contained grease-free aluminium powder to reveal internal motion. Drops heavier than water were formed from open tubes, and those lighter than water entered the foot of the column through various sized nozzles connected by cone and socket joints to a vertical stand pipe 130 cm high and surmounted by a reservoir.

The densities of indene, tetralin and 1 methyl naphthalene were so close to that of water that measurement of interfacial tensions by any of the normal methods proved rather difficult: accordingly, for qualitative indications, values were estimated by Antonoffs' rule for these three substances. Transition velocities at which circulation began – measured by stopwatch – are shown in Table 2. While the values do not show a close correlation, they do support our earlier finding [8] that circulation occurs less readily the higher the interfacial tension of the system.

Modification of Circulation by Trace Components

A particular specimen of nitrobenzene, supplied as "pure," was used to form droplets containing aluminium particles falling through distilled water in a glass column 5 cm in diameter. The circulation currents within the droplets (as revealed by the aluminium particles) tended to damp out, motion ceasing first at the rear pole and progressively decaying towards the leading pole of the drop, becoming entirely stagnant after 115-125 cm of fall. (Droplet formation effects were eliminated by gently pouring the drops from a glass spoon held beneath the water surface.) This "pure" nitrobenzene was shaken with sodium carbonate and redistilled, whereupon three important changes were seen:–

(1) The droplets showed constant and more rapid internal circulation over the whole length of fall (143 cm).

(2) Droplets of about 0·5 cm diameter were about twice as oblate as those before redistillation. This was probably a centrifugal effect due to greatly increased circulation speed, since determinations by the drop weight method showed the interfacial tension against water to be identical before and after distillation.

(3) Drops of redistilled nitrobenzene about

Table 2.

	density gms/cc	*viscosity 20°C centistokes*	*interfacial tension dynes/cm 20°C*	*transition velocity cms/sec*
Benzyl alcohol	$1{\cdot}043\ \frac{20}{4}$	5·58	4·75	< 0·7
Benzaldehyde	$1{\cdot}046\ \frac{20}{4}$	c.a. 1·5	15·5	< 1·3
Indene	$1{\cdot}006\ \frac{20}{4}$	1·78	26*	2·4–3
Tetralin	$0{\cdot}973\ \frac{18}{4}$	2·2	37*	3·2–3·4
1 methyl naphthalene	$1{\cdot}025\ \frac{14}{4}$	3·4	34*	c.a. 4·2
Cetane	$0{\cdot}774\ \frac{20}{4}$	3·6	35	> 14·5

* Calculated from surface tension by Antonoff's rule.

0·5 cm in diameter had a terminal velocity about 25% greater than for similar size drops before redistillation (see later).

The residue from the distillation was somewhat discoloured, but gave completely stagnant droplets.

The refractive index of the redistilled nitrobenzene at 20·2°C was 1·5523 compared with the value in International Critical Tables [12] at 20°C of 1·5529. The refractive index of the nitrobenzene both before and after distillation was the same.

Evidently the impurity inhibiting circulation is a relatively high-boiling substance, present only in extremely small concentration.

Inhibiting Effect of a Surface Active Agent on Circulation Behaviour

A curve of drop size versus fall velocity was experimentally determined, and drop sizes were estimated from fall velocities. These drops had a velocity of 13·6 cm/sec and a diameter of approximately 0·53 cm. They were formed beneath the surface of the water from a narrow glass tube, allowed to hang a moment to become stagnant, and then detached by a sideways jerking of the tube. This prevented any tendency to circulate due to formation effects.

The disperse phase consisted of the "pure" nitrobenzene without redistillation. To the continuous phase – distilled water – were added various concentrations (0·0005% to 0·01% by weight) of dodecyl sodium sulphate 6. Even very small concentrations of this additive inhibited circulation, since the length of fall required to damp out circulation completely was reduced, as shown by Fig. 3.

Diffusing Solute overcomes effects of a Surface-Active Agent

In these experiments the continuous phase was distilled water containing 0·01% by weight of dodecyl sodium sulphate 6. The disperse phase was the "pure" nitrobenzene without redistillation, and

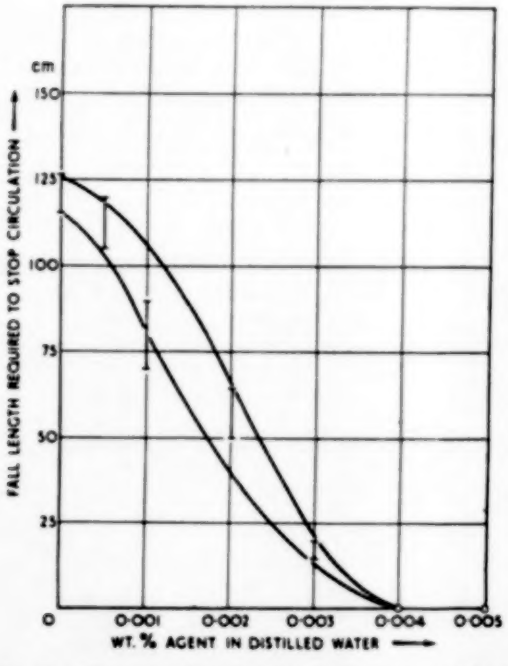

Fig. 3 Disperse phase "pure" nitrobenzene without redistillation.

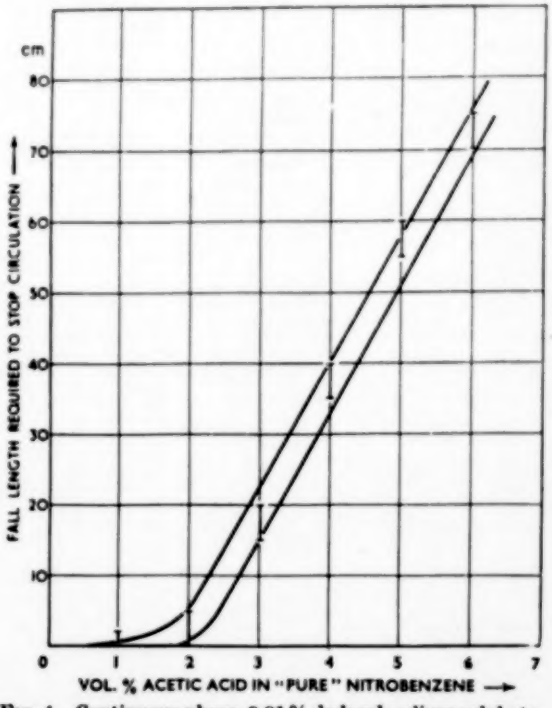

Fig. 4 Continuous phase, 0·01% dodecyl sodium sulphate 6 in distilled water.

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contained various concentrations (up to 6% by volume) of acetic acid. The drops had a velocity of 12·9 cm/sec and a diameter of approximately 0·47 cm.

Whereas acid-free nitrobenzene droplets had been completely stagnant at this surface-active agent concentration, the presence of the acetic acid overcame the inhibiting effects of the agent and promoted circulation as shown in Fig. 4.

Droplets of pure benzyl alcohol falling through distilled water, (solubility 4%) showed circulation (revealed by aluminium particles) almost immediately after detachment; but when they were formed from a glass tube previously dipped in a 0·5% aqueous solution of sodium dodecyl sulphate 6, circulation began only after about 30 cm of fall, due to the time required for dissolution of the surface layer of alcohol plus adsorbed film.

STRUCTURE OF THE ADSORBED FILM

At very low concentrations of surface-active material the circulating motion of the interface may cause the adsorbed molecules to accumulate at the rear of the drop surface, giving a coherent film which progressively extends over the interface until circulaton is stopped. This assumes that the rate of accumulation exceeds the rate of desorption from the film.

The aqueous bulk concentrations of sodium dodecyl sulphate 6 in equilibrium with various concentrations at a static interface, have been calculated below for tentative analogy with conditions at the droplet interface.

The dodecyl chain is assumed to lie flat near the plane of the interface and to be a cylinder [3] about 13·8°A in length and 20·5°A^2 in cross-section [1]. The Gibbs adsorption equation for dilute solutions is $-S = \frac{C}{iRT}\frac{d\gamma}{dC}$ where the interfacial tension, γ, is in dynes/cm and the bulk concentration, C, in gm.mols/litre. According to ADDISON [2], S approximates to the amount of solute in a layer one molecule deep on unit surface. For the concentration range 0 to 0·5% (weight), $\frac{d\gamma}{dC}$ was experimentally measured as $-6{,}370$ in the nitrobenzene-water system, the Avogadro number is $6{\cdot}023 \times 10^{23}$ and i lies between 1 and 2, depending upon the degree of ionisation of adsorbate [7] and upon the relative interfacial concentrations of anion and cation [16]. Water temperature was 20°C.

Three types of static film structure may then be postulated :–

(1) The maximum interfacial concentration possible without mutual interference between adsorbed molecules corresponds to their forming the diameters of hexagonally close-packed circles [3].

(2) Higher concentrations lead to increasing interference until a layer of tightly packed dodecyl chains lying flat near the interface is formed.

(3) Further adsorption is accomplished by the two hydrophobic portions of the molecule assuming an orientation more and more nearly normal to the interface, leading to a " condensed monolayer " at saturation.

The calculated film and bulk concentrations corresponding to these three types of structure appear in Table 3.

Table 3.

Film structure	*Interfacial concentration gm.mols/cm²*	*Equilibrium bulk concentration gm.mols/litre*	
		$i = 1$	$i = 2$
1	$< 1{\cdot}007 \times 10^{-10}$	< 0·000385	< 0·00077
2	$1{\cdot}007 \times 10^{-10}$ to $2{\cdot}36 \times 10^{-10}$ >	0·000385–0·000905	0·00077–0·00181
3	$> 2{\cdot}36 \times 10^{-10}$	> 0·000905	> 0·00181

Consider the bulk concentration of 0·003% (weight) (0·000104 gm.mols/litre). If the transition between types 1 and 2 films prevents circulation, then, assuming $i = 1$, the bulk and interfacial concentrations require increasing 0·000385/0·000104 = 3·7 times to permit this film structure. If the desorption rate from the interface is low, the time required for adsorption negligible and the droplet begins circulating at maximum speed (i.e. renews its surface while falling one diameter) then, by the "accumulation mechanism," this increase in interfacial concentration will be achieved after travelling 3·7 drop diameters from the nozzle (about 2 cm for a drop 0·55 cm in diameter). The calculated distances of fall required to stop circulation based on various assumptions, are compared with the experimental values in Table 4 below.

The assumptions made must lead to some inaccuracies, but assuming the validity of applying the Gibbs equation to these experiments, then the calculated values are probably too small because the drops circulate well below the maximum possible speed [10] and because the time required for adsorption is appreciable in relation to the time of fall.

Some Factors affecting Fall Velocities in Liquid-Liquid Systems

Droplets were formed with a 25 cc burette fitted for constant head by use of a tightly fitting rubber bung through which passed a thin-walled glass tube, admitting a stream of air to a point below the level of the liquid in the burette. Five or six glass nozzles of various internal diameters were attached in turn to the burette with hard polythene tubing, and drop sizes were known from the volume of dispersed phase required to form a given number of drops. The drops fell through a glass column of 4 cm internal diameter and height 142 cm, fall velocities being measured by stopwatch. Three systems were studied :–

(*a*) Redistilled "pure" nitrobenzene, falling in distilled water.

(*b*) "Pure" nitrobenzene referred to earlier, without redistillation, in distilled water.

(*c*) Redistilled "pure" nitrobenzene, falling in 0·003% (weight) solution of sodium dodecyl sulphate 6 in distilled water.

The presence or absence of internal circulation was determined by the addition of aluminium particles to the drops, in parallel experiments, to duplicate the experimental conditions for each drop size.

Discussion

Fluid droplets differ from rigid spheres in three ways during free fall.

(1) The frictional drag of the surrounding fluid may induce circulation of both the interface and interior of the droplets.

Table 4.

Aqueous concentration of sodium dodecyl sulphate 6 % *(weight)*	*Calculated fall distances for transition between types 1 and 2 films at the interface* cm		*Calculated fall distances for transition between types 2 and 3 films at the interface* cm		*Experimental distance of fall required to stop circulation* cm
	$i = 1$	$i = 2$	$i = 1$	$i = 2$	
0·004	1·5	3·0	3·6	7·2	0–0·5
0·003	2·0	4·0	4·8	9·6	15–20
0·002	3·0	6·0	7·2	14·4	50–65
0·0005	12·2	24·4	28·6	57·2	105–120

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(2) The drop may depart from spherical shape, assuming some oblateness, due to gravity.

(3) Prolate-oblate type of oscillation may occur.

In Fig. 5, the experimental curves, 1, 2 and 3, corresponding to systems (*a*), (*b*) and (*c*), are compared with the predicted curve for rigid spheres of the same density, curve 4, using the data of DAVIES [6]. Shaded and unshaded points denote oscillating and non-oscillating drops respectively. The experiments with aluminium particles showed that for curve 3 all drops were internally stagnant; for curve 2 all drops showed weak internal circulation, while all drops of curve 1 showed vigorous internal circulation. Also, all except the smallest drops of curve 1 showed vigorous oblate-near prolate oscillation; whereas all drops of curves 2 and 3 had no such oscillation, but possessed a degree of oblateness which increased with drop size. Drops for all three curves fell with their major axis normal to the direction of motion.

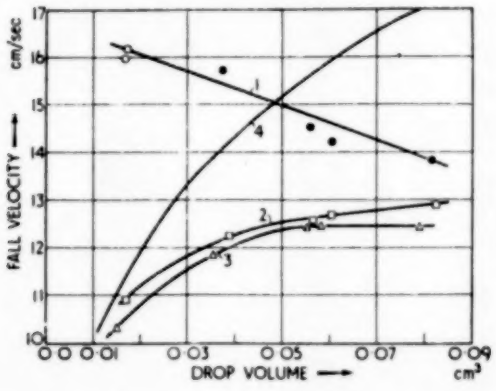

FIG. 5

Effects of oblateness on fall velocity

Curves 2 and 3 fall further below the predicted curve for rigid spheres as drop size increases, presumably due to increasing form drag with the observed increase in oblateness.

Effects of internal circulation on fall velocity

The weak circulation within drops of curve 2 evidently reduces the total drag sufficiently to cause all these drops to fall some 2-4% faster than the stagnant drops of curve 3.

The unshaded points of curve 1 correspond to drops of volume c.a. 0·017 cc; they showed vigorous internal circulation but no detectable oscillation. They fall about 40% faster than predicted for a rigid sphere of the same density and size, and about 50% faster than the drop of the same density and size in curve 3, this latter drop being completely stagnant.

Effects of oscillation on fall velocity

Since all 4 curves must pass through the origin, then a maximum fall velocity is reached for drops of curve 1, below a drop size of 0·02 cc. Above this drop size oscillation of the drop occurs, reducing the fall velocity. The extent of this oscillation increases with drop size. If we assume that, in the absence of oscillation, curve 1 would have flattened off at larger drop sizes in a similar manner to curve 2 or 3, then curve 1 shows that, for a 0·08 cc drop, the oscillation occurring in this system reduced the fall velocity by at least 12%.

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On the steady state fractionation of multicomponent and complex mixtures in an ideal cascade

Part IV. The calculation of the minimum reflux ratio

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(*Received* 26 *January*, 1955)

Summary—In this paper formulae for calculating the minimum reflux in rectification are summarized and developed for complex mixtures which are characterised by continuous or semi-continuous distribution functions. Two numerical examples are considered, one for continuous and one for semi-continuous mixtures.

Résumé—Dans cet article, les auteurs résument et développent des formules permettant le calcul du reflux minimum dans la rectification de mélanges complexes caractérisés par des fonctions de distribution continues ou semi-continues. Ils examinent deux examples numériques : un pour les mélanges continus et un pour les mélanges semi-continus.

INTRODUCTION

In a preceding paper the present authors presented a solution, in closed form, of the equations for the separation of complex mixtures, that is, mixtures with an indefinite number of components, in an ideal column. In this paper will be summarized the solution to the minimum reflux problem for complex mixtures, together with two illustrative examples.

First of all, it is to be noted that at any given reflux ratio the separation of a feed of known composition and heat content is completely specified if two and only two points of the distribution function of the overhead product are fixed *a priori*, provided, of course, that the feed is introduced at the optimum location in the column. The above is but another formulation of the well-known theorem that, for any multicomponent or complex mixture, the number of degrees of freedom in a distillation column is equal to 2. Secondly, it will be recalled that for a specified separation of a given feed, as the reflux ratio approaches its minimum permissible value, both N and S, the number of plates in the enriching and the stripping sections of the column, respectively, increase beyond limit. Finally, use will be made of the following theorem, which was rigorously proved, and which forms the basis for this discussion of the minimum reflux problem.

THEOREM :

At minimum reflux, and for a specified separation of a feed of known composition and heat content, there exist two values of p, namely $p = h$ and $p = l$, such that :

(a) $x_0(p) > 0$, if $x_F(p) > 0$, for $p < h$

(b) $\lim_{N\to\infty} \dfrac{x_0(p)}{x_0(h)} \left(\dfrac{p}{h}\right)^N$ exists for $p > h$

(c) $x_0^*(p) > 0$, if $x_F(p) > 0$, for $p > l$

(d) $\lim_{S\to\infty} \dfrac{x_0^*(p)}{x_0^*(l)} \left(\dfrac{l}{p}\right)^S$ exists for $p < l$

where $x_0(p)$, $x_F(p)$ and $x_0^*(p)$ are, respectively, the distribution functions of the overhead product, the feed and the bottom product. Following a well-established tradition, the point

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h will be referred to as the heavy key component and l as the light key component.

The minimum reflux problem, then, under the assumptions of ideal plates, constant molal overflow and constant relative volatilities throughout the column, can be solved exactly for continuous mixtures as follows :

First it is supposed, for simplicity, that the distribution function $x_F(p)$ is everywhere positive on the positive p-axis. Then the following functions are defined :

$$\text{(a) } w_F(\lambda) \equiv -q - P\int_0^\infty \frac{p x_F(p)}{\lambda - p_i}\,dp \text{ for } l \leqq \lambda \leqq h \quad (1)$$

where the symbol P in front of an improper integral denotes its Cauchy principal value and q represents the thermal condition of the feed.

$$\text{(b) } \rho(\lambda) \equiv \frac{1}{\pi}\tan^{-1}\frac{\pi\lambda x_F(\lambda)}{w_F(\lambda)} \text{ for } l \leqq \lambda \leqq h \quad (2)$$

$$\text{(c) } B(p) = \rho(p)\exp\left\{P\int_l^h \frac{\rho(\lambda)}{\lambda - p}\,d\lambda - \sum_1^\infty \frac{[\rho(p)]^{2i}}{i}\zeta(2i)\right\} \quad (3)$$

for $l \leqq p \leqq h$, where $\zeta(2i)$ is the Riemann zeta function [1]. However, if $\rho(p)$ is close to unity, then it is better to rearrange eq. (3) into the more convenient form

$$B(p) = \rho(p)\left[1 - (\rho(p))^2\right]\exp\left\{P\int_l^h \frac{\rho(\lambda)}{\lambda - p}\,d\lambda - \sum_1^\infty \frac{[\rho(p)]^{2i}}{i}(\zeta(2i) - 1)\right\} \quad (4)$$

for $l \leqq p \leqq h$.

$$\text{(d) } B(p) = \exp\left\{P\int_l^h \frac{\rho(\lambda)}{\lambda - p}\,d\lambda\right\} \text{ for } p < l \quad (5)$$

Then,

$$D\,p\,x_0(p) = B(p)\left\{RD + \int_0^l \frac{\lambda x_F(\lambda)}{B(\lambda)(\lambda - p)}\,d\lambda\right\} \quad (6)$$

for $l \leqq p \leqq h$, and

$$RD = \int_0^l \frac{\lambda x_F(\lambda)}{B(\lambda)(l - \lambda)}\,d\lambda \quad (7)$$

while

$$D = \int_0^\infty D\,x_0(p)\,dp = \int_0^l x_F(p)\,dp + \int_l^h D\,x_0(p)\,dp \quad (8)$$

Equations (6), (7) and (8) enable one to calculate not only the minimum reflux ratio but the distribution function of the overhead product as well. Moreover, the relations

$$RD = \int_0^l \frac{p\,x_F(p)}{h - p}\,dp + \int_l^h \frac{p\,D\,x_0(p)}{h - p}\,dp \quad (9)$$

and

$$Dpx_0(p) = \frac{1}{\pi}\tan\pi\rho(p)\left\{RD - P\int_0^\infty \frac{\lambda}{p - \lambda}\frac{Dx_0(\lambda)}{d\lambda}\,d\lambda = \frac{w(p)}{\pi}\tan\pi\rho(p)\right. \quad (10)$$

for $l \leqq p \leqq h$

can be used as a check in any numerical calculation.

It is clear from the above formulae that the minimum reflux problem, for any desired separation of the feed, can be easily solved if the two points h and l, that is, the two key components, can be spotted in advance. Since this cannot be accomplished readily in most cases, it appears preferable to assume values for h and l until the calculated separation of the feed becomes essentially identical with that specified in the problem.

This brief presentation of the analytic method for solving the minimum reflux problem has been restricted to continuous mixtures for which the distribution function was positive along the positive p-axis.

Illustrative Examples

(a) *Continuous Mixtures.*

Let us suppose that the distribution function of the feed, $x_F(p)$ is given by

$$x_F(p) = \frac{4}{\sqrt{\pi}}(p - 1)^2 e^{-(p-1)^2} \text{ for all } p > 1$$

and $x_F(p) = 0$ for $p < 1$. The vapour-to-liquid

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Table II. Numerical values for $w_F(\lambda)$, tan $\pi\rho(\lambda)$ and $\rho(\lambda)$.

λ	$w_F(\lambda)$	tan $\pi\rho(\lambda)$	$\rho(\lambda)$	λ	$w_F(\lambda)$	tan $\pi\rho(\lambda)$	$\rho(\lambda)$
1·45	3·1968	0·5318	0·1556	2·30	− 1·5878	− 3·2026	0·5964
1·50	3·2347	0·6401	0·1812	2·35	− 1·9376	− 2·5329	0·6197
1·55	3·2213	0·7626	0·2074	2·40	− 2·2562	− 2·0821	0·6426
1·60	3·1539	0·9034	0·2339	2·45	− 2·5406	− 1·7560	0·6648
1·65	3·0315	1·0686	0·2606	2·50	− 2·7888	− 1·5072	0·6865
1·70	2·8548	1·2674	0·2874	2·55	− 3·0000	− 1·3102	0·7075
1·75	2·6261	1·5143	0·3142	2·60	− 3·1741	− 1·1493	0·7280
1·80	2·3493	1·8332	0·3410	2·65	− 3·3119	− 1·0149	0·7476
1·85	2·0306	2·2654	0·3677	2·70	− 3·4151	− 0·9003	0·7667
1·90	1·6729	2·9015	0·3944	2·75	− 3·4856	− 0·8012	0·7850
1·95	1·2867	3·9327	0·4207	2·80	− 3·5261	− 0·7144	0·8026
2·00	0·8788	5·9358	0·4469	2·85	− 3·5394	− 0·6376	0·8193
2·05	0·4571	11·6400	0·4727	2·90	− 3·5286	− 0·5690	0·8353
2·10	0·0296	181·4916	0·4983	2·95	− 3·4970	− 0·5075	0·8505
2·15	− 0·3957	− 13·5750	0·5234	3·00	− 3·4477	− 0·4520	0·8649
2·20	− 0·8114	− 6·5588	0·5482	3·05	− 3·3837	− 0·4017	0·8784
2·25	− 1·2107	− 4·3154	0·5725				

Table III. Numerical values of $\rho(\lambda)$ at shorter intervals of λ

λ	$\rho(\lambda)$	λ	$\rho(\lambda)$	λ	$\rho(\lambda)$
1·450	0·1556	2·00	0·4469	2·55	0·7075
1·475	0·1683	2·025	0·4598	2·575	0·7178
1·50	0·1812	2·05	0·4727	2·60	0·7280
1·525	0·1943	2·075	0·4856	2·625	0·7378
1·550	0·2074	2·10	0·4983	2·65	0·7476
1·575	0·2206	2·125	0·5109	2·675	0·7573
1·60	0·2339	2·15	0·5234	2·70	0·7667
1·625	0·2472	2·175	0·5359	2·725	0·7759
1·65	0·2606	2·20	0·5482	2·75	0·7850
1·675	0·2740	2·225	0·5604	2·775	0·7939
1·70	0·2874	2·25	0·5725	2·80	0·8026
1·725	0·3008	2·275	0·5845	2·825	0·8110
1·75	0·3142	2·30	0·5964	2·85	0·8193
1·775	0·3276	2·325	0·6081	2·875	0·8274
1·80	0·3410	2·35	0·6197	2·90	0·8353
1·825	0·3543	2·375	0·6313	2·925	0·8430
1·85	0·3677	2·40	0·6426	2·95	0·8505
1·875	0·3811	2·425	0·6538	2·975	0·8578
1·90	0·3944	2·45	0·6648	3·00	0·8649
1·925	0·4075	2·475	0·6758	3·025	0·8717
1·95	0·4207	2·50	0·6865	3·05	0·8784
1·975	0·4339	2·525	0·6970		

ratio in the feed is equal to 1. It is desired to determine the minimum reflux ratio and the two points $p = \beta$ and $p = \beta^*$ such that

$$\frac{x_0(\beta)}{x_0^*(\beta)} = 20 \text{ and } \frac{x_0^*(\beta^*)}{x_0(\beta^*)} = 20$$

It is also specified that

$$h = 3{\cdot}05 \text{ and } l = 1{\cdot}45.$$

The above is a somewhat simplified problem, since one usually does not specify h and l, but

Table IV. Numerical values for $B(\lambda)$, $1{\cdot}45 < \lambda \leqslant 3{\cdot}05$

λ	$B(\lambda)$	λ	$B(\lambda)$
1·50	0·72012	2·30	0·59574
1·55	0·76360	2·35	0·53131
1·60	0·81799	2·40	0·46740
1·65	0·86952	2·45	0·40611
1·70	0·91224	2·50	0·34774
1·75	0·94416	2·55	0·29324
1·80	0·96436	2·60	0·24303
1·85	0·97220	2·65	0·19808
1·90	0·96659	2·70	0·15772
1·95	0·94956	2·75	0·12238
2·00	0·92096	2·80	0·09186
2·05	0·88237	2·85	0·066038
2·10	0·83525	2·90	0·04400
2·15	0·78162	2·95	0·02664
2·20	0·72245	3·00	0·01221
2·25	0·66004		

β and β^* instead; however, it will suffice as an example. Some of the results are presented in Tables I-V. Table I will be found in the previous paper, Part 3. The method of calculating Cauchy principle values of integrals was also discussed in Part 3.

It can be shown now from eq. (3) that in any small interval $\Delta\lambda$, the function

$$\frac{\lambda x_F(\lambda)}{B(\lambda)\,(1{\cdot}45 - \lambda)}$$

Table V. Numerical values for $B(\lambda)$ *and* $\dfrac{\lambda x_F(\lambda)}{B(\lambda)\,(1{\cdot}45 - \lambda)}$ *for* $1{\cdot}00 \leqslant \lambda < 1{\cdot}45$.

λ	$\lambda x_F(\lambda)$	$B(\lambda)$	$\lambda x_F(\lambda)/B(\lambda)\,(1{\cdot}45 - \lambda)$
1·44375	0·52696	5·26775	16·005600
1·4375	0·51287	4·67410	8·77840
1·43125	0·49889	4·32640	6·14987
1·425	0·48503	4·10071	4·73120
1·40	0·43077	3·54360	2·43120
1·35	0·33019	3·02391	1·09193
1·30	0·24132	2·72976	0·58935
1·25	0·16563	2·52797	0·32760
1·20	0·10408	2·37669	0·17517
1·15	0·05710	2·25696	0·08433
1·10	0·02458	2·15937	0·03253
1·05	0·00591	2·07773	0·00711

can be represented as $K/(1{\cdot}45 - \lambda)^{\alpha}$ where both K and α vary slowly with λ. It is found then that for

$1{\cdot}44375 \leqq \lambda \leqq 1{\cdot}45, \quad \alpha = 0{\cdot}8444 = 1 - \rho(1{\cdot}45)$
$1{\cdot}4375 \leqq \lambda \leqq 1{\cdot}44375, \alpha = 0{\cdot}86656$
$1{\cdot}425 \leqq \lambda \leqq 1{\cdot}4375, \alpha = 0{\cdot}89174$
$1{\cdot}40 \leqq \lambda \leqq 1{\cdot}425, \alpha = 0{\cdot}95313$

Therefore, from eq. (7)

$$RD = \int_0^{1{\cdot}45} \frac{\lambda x_F(\lambda)}{B(\lambda)\,(1{\cdot}45 - \lambda)}\,d\lambda = 1{\cdot}04971$$

The function $p\,D x_0(p)$ can next be calculated from eq. (6) and must be identical with that given by eq. (10), namely

$$[\lambda\,Dx_0(\lambda)]_{\text{calc.}} = \frac{w(\lambda)}{\pi}\tan\pi\rho(\lambda)$$

This comparison is made in Table VI.

Finally, from eq. (9)

$$(RD)_{\text{calc.}} = 1{\cdot}04895$$

Also

$$D = \int_0^{\infty} D x_0(p)\,dp = 0{\cdot}50991$$

and therefore

$$R_{\text{min.}} = 2{\cdot}0586$$

Table VI.

λ	$\lambda\,Dx_0(\lambda)$	$[\lambda\,Dx_0(\lambda)]_{\text{calc.}}$	λ	$\lambda\,Dx_0(\lambda)$	$[\lambda\,Dx_0(\lambda)]_{\text{calc.}}$
1·50	0·62490	0·62041	2·30	0·60968	0·61095
1·55	0·70417		2·35	0·54445	
1·60	0·77695	0·77469	2·40	0·47950	0·48074
1·65	0·84099		2·45	0·41706	
1·70	0·89325	0·89120	2·50	0·35745	0·35829
1·75	0·93286		2·55	0·30169	
1·80	0·95940	0·95856	2·60	0·25022	0·25104
1·85	0·97247		2·65	0·20410	
1·90	0·97117	0·96932	2·70	0·16262	0·16372
1·95	0·95741		2·75	0·12628	
2·00	0·93160	0·92818	2·80	0·09484	0·09539
2·05	0·89493		2·85	0·06820	
2·10	0·84901		2·90	0·04547	0·04682
2·15	0·79615		2·95	0·02758	
2·20	0·73718	0·74109	3·00	0·01269	0·01324
2·25	0·67455				

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It is seen then from Table VI that, on the whole, the agreement between $\lambda\, Dx_0(\lambda)$ and $[\lambda\, Dx_0(\lambda)]_{calc.}$, as well as between RD and $(RD)_{calc.}$, is very satisfactory. It was hoped moreover that by means of eq. (10) one could have obtained even more accurate values for $\lambda\, Dx_0(\lambda)$ by applying an iterative method. Various attempts to discover the appropriate iteration were not successful, however, and the Seidel method, which is the most commonly used in such cases, did seem to diverge, in spite of the close agreement between $\lambda\, Dx_0(\lambda)$ and $[\lambda\, Dx_0(\lambda)]_{calc.}$. It appears therefore that the best way to improve the accuracy of the results would be to increase the accuracy of the previous calculations.

It is necessary to obtain the two components β and β^*. This can be done with the aid of Table VI, and it is estimated that

$$\beta \sim 1{\cdot}495$$

and

$$\beta^* \sim 2{\cdot}9524$$

In this problem then the two "key components" were specified a priori and then β and β^* were determined; it is much more common, however, in practice to specify β and β^*, and then to calculate the minimum reflux. The procedure adopted here however appears quite straightforward, and therefore it should be used even when h and l are not known. In other words, when β and β^* are specified, one assumes different values for h and l and evaluates the corresponding $R_{min.}$, β and β^*; the desired answer can then be obtained by a proper interpolation.

(b) *Semi-continuous Mixtures.*

It is supposed that the distribution function of the feed, $x_F(p)$, is now given by

$$x_F(p) = \frac{3}{\sqrt{\pi}}(p-1)^2 e^{-(p-1)^3} \quad \text{for all} \quad p > 1$$

and $x_F(p) = 0$ for $p < 1$. It is also supposed that one component is present, at $p = 2\,50$, in finite amounts, and that its mole fraction in the feed, $x_F(i)$, is equal to 0·25. The vapour to liquid ratio in the feed is again taken equal to 1. It is desired to determine the minimum reflux ratio, and the two points $p = \beta$ and $p = \beta^*$, such that

$$\frac{x_0(\beta)}{x_0^*(\beta)} = 20 \text{ and } \frac{x_0^*(\beta^*)}{x_0(\beta^*)} = 20$$

It is also specified that

$$h = 3{\cdot}05 \text{ and } l = 1{\cdot}45$$

This problem then is quite similar to that worked out earlier, except for the presence of the distinguishable component at $p = 2{\cdot}50$. The function $\rho(\lambda)$ must now be determined from

$$\lambda\, x_F(\lambda)\, \pi \cot \pi\rho(\lambda) = -0{\cdot}50 - \frac{0{\cdot}6250}{\lambda - 2{\cdot}50} - P\int_{1{\cdot}0}^{\infty} \frac{q\, x_F(q)}{\lambda - q}\, dq \equiv w_F(\lambda)$$

so that

$$\rho(\lambda) = \frac{1}{\pi}\tan^{-1}\frac{\pi\,\lambda\, x_F(\lambda)}{w_F(\lambda)}$$

Numerical results are given in Tables VII-X.

So far, equations (1)-(10) have been used with only one modification. However, the following changes are necessary, now that one distinguishable component is present in the mixture:

(a) Instead of eq. (8)

$$D = \int_0^{\infty} D\, x_0(p)\, dp + D\, x_0(i) \qquad (11)$$

(b) Instead of eqs. (9) and (10), respectively,

$$RD = \int_0^{3{\cdot}05} \frac{p\, D\, x_0(p)}{3{\cdot}05 - p}\, dp + \frac{2{\cdot}50\, D\, x_0(i)}{3{\cdot}05 - 2{\cdot}50} \qquad (12)$$

and

$$D\, p\, x_0(p) = \frac{1}{\pi}\tan \pi\rho(p)\left\{RD - \frac{2{\cdot}50\, D\, x_0(i)}{2{\cdot}50 - p} - P\int_0^{\infty} \frac{\lambda\, D\, x_0(\lambda)}{p - \lambda}\, d\lambda\right\} \equiv \frac{w(p)}{\pi}\tan \pi\rho(p) \text{ for } l \leq p \leq h \qquad (18)$$

where $x_0(i)$ is the mole fraction of the distinguishable component in the overhead product and is given by

Table VII. Numerical values for $w_F(\lambda)$, tan $\pi\,\rho\,(\lambda)$ *and* $\rho(\lambda)$.

λ	$w_F(\lambda)$	tan $\pi\rho(\lambda)$	$\rho(\lambda)$	λ	$w_F(\lambda)$	tan $\pi\rho(\lambda)$	$\rho(\lambda)$
1·45	3·8238	0·4446	0·1332	2·30	2·4122	2·1081	0·3590
1·50	3·9014	0·5307	0·1553	2·35	3·4512	1·4220	0·3049
1·55	3·9319	0·6248	0·1777	2·40	5·9104	0·7948	0·2138
1·60	3·9132	0·7281	0·2003	2·45	13·9594	0·3196	0·0985
1·65	3·8453	0·8424	0·2228	2·50			
1·70	3·7298	0·9700	0·2452	2·55	− 19·833	− 0·1982	0·9377
1·75	3·5706	1·1137	0·2671	2·60	− 11·6741	− 0·3125	0·9036
1·80	3·3731	1·2768	0·2885	2·65	− 9·3721	− 0·0342	0·8866
1·85	3·1460	1·4626	0·3091	2·70	− 7·7484	− 0·3968	0·8798
1·90	2·8951	1·6766	0·3288	2·75	− 6·9856	− 0·3998	0·8789
1·95	2·6352	1·9203	0·3472	2·80	− 6·4705	− 0·3892	0·8818
2·00	2·3788	2·1929	0·3638	2·85	− 6·0870	− 0·3707	0·8870
2·05	2·1423	2·4831	0·3782	2·90	− 5·7786	− 0·3475	0·8936
2·10	1·9463	2·7603	0·3894	2·95	− 5·5155	− 0·3218	0·9009
2·15	1·8186	2·9538	0·3961	3·00	− 5·2810	− 0·2951	0·9087
2·20	1·7997	2·9569	0·3962	3·05	− 5·0655	− 0·2683	0·9166
2·25	1·9559	2·6712	0·3860				

Table VIII. Numerical values of $\rho(\lambda)$ *at shorter intervals of* λ.

λ	$\rho(\lambda)$	λ	$\rho(\lambda)$	λ	$\rho(\lambda)$
1·450	0·1332	2·000	0·3638	2·550	0·9377
1·475	0·1442	2·025	0·3714	2·575	0·9185
1·500	0·1553	2·050	0·3782	2·600	0·9036
1·525	0·1665	2·075	0·3843	2·625	0·8938
1·550	0·1777	2·100	0·3894	2·650	0·8866
1·575	0·1890	2·125	0·3936	2·675	0·8824
1·600	0·2003	2·150	0·3961	2·700	0·8798
1·625	0·2116	2·175	0·3974	2·725	0·8789
1·650	0·2228	2·200	0·3962	2·750	0·8789
1·675	0·2340	2·225	0·3932	2·775	0·8801
1·700	0·2452	2·250	0·3860	2·800	0·8818
1·725	0·2562	2·275	0·3759	2·825	0·8842
1·750	0·2671	2·300	0·3590	2·850	0·8870
1·775	0·2779	2·325	0·3366	2·875	0·8902
1·80	0·2885	2·350	0·3049	2·900	0·8936
1·825	0·2989	2·375	0·2624	2·925	0·8972
1·850	0·3091	2·400	0·2138	2·950	0·9009
1·875	0·3191	2·425	0·1540	2·975	0·9048
1·900	0·3288	2·450	0·0985	3·000	0·9087
1·925	0·3382	2·475	0·0513	3·025	0·9126
1·950	0·3472	2·500		3·050	0·9166
1·975	0·3558	2·525	0·9653		

$$x_0(i) = x_F(i)\,\frac{x_0(2\cdot5)}{x_F(2\cdot5)} = 0\cdot25\,\frac{x_0(2\cdot5)}{x_F(2\cdot5)} \qquad (14)$$

Table IX. Numerical values for $B(\lambda)$, $1\cdot45 < \lambda < 3\cdot05$.

λ	$B(\lambda)$	λ	$B(\lambda)$	λ	$B(\lambda)$
1·50	0·50599	2·05	0·63631	2·65	0·14282
1·55	0·54193	2·10	0·60266	2·70	0·11341
1·60	0·58356	2·15	0·56387	2·75	0·08774
1·65	0·62204	2·20	0·52136	2·80	0·06568
1·70	0·65420	2·25	0·47614	2·85	0·04701
1·75	0·67825	2·30	0·42897	2·90	0·03144
1·80	0·69353	2·35	0·38081	2·95	0·01868
1·85	0·69944	2·40	0·33607	3·00	0·00842
1·90	0·69622	2·45	0·29813		
1·95	0·68417	2·55	0·21817		
2·00	0·66383	2·60	0·17663		

So, it is found from eq. (7) that

$$RD = \int_0^{1\cdot45} \frac{q\,x_F(q)}{B(q)\,(1\cdot45 - q)}\,dq = 1\cdot10911$$

Next, the function $p\,D\,x_0(p)$ can be calculated from eq. (6), and must, moreover, be identical with that obtained from eq. (13), namely

$$\left[\lambda\,D\,x_0(\lambda)\right]_{\text{calc.}} = \frac{w(\lambda)}{\pi}\tan\pi\rho(\lambda)$$

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Table X. Numerical values for $B(\lambda)$ and $\dfrac{\lambda x_p(\lambda)}{B(\lambda)(1{\cdot}45-\lambda)}$ for $1{\cdot}00 \leqslant \lambda < 1{\cdot}45$.

λ	$\lambda x_p(\lambda)$	$B(\lambda)$	$\lambda x_p(\lambda)/B(\lambda)(1{\cdot}45-\lambda)$
1·4375	0·38465	3·74617	8·21424
1·425	0·36377	3·35040	4·34300
1·4125	0·34343	3·12677	2·92893
1·400	0·32308	2·96894	2·17640
1·35	0·24764	2·57535	0·96158
1·30	0·18099	2·36251	0·51073
1·25	0·12422	2·21483	0·28043
1·20	0·07806	2·10266	0·14850
1·15	0·04283	2·01340	0·07091
1·10	0·01844	1·93962	0·02716
1·05	0·00443	1·87789	0·00590

and $[\lambda\, Dx_0(\lambda)]_{\text{calc.}}$, as well as between RD and $(RD)_{\text{calc.}}$, is very satisfactory. As was said earlier, in connection with the first problem, the agreement between the two functions could not be improved by any interative method, and again it was found that the Seidel method diverged. So it appears that more accurate results could be obtained only by increasing the accuracy of the calculations.

Finally, the two components β and β^* can be estimated from Table XI. It is found that

$$\beta \sim 1{\cdot}496$$

and

$$\beta^* \sim 2{\cdot}949$$

It is hoped then that the example just presented

Table XI.

λ	$\lambda\, Dx_0(\lambda)$	$[\lambda\, Dx_0(\lambda)]_{\text{calc.}}$	λ	$\lambda\, Dx_0(\lambda)$	$[\lambda\, Dx_0(\lambda)]_{\text{calc.}}$
1·50	0·47925	0·47867	2·30	0·46554	0·47127
1·55	0·54048		2·35	0·41399	
1·60	0·59566	0·59480	2·40	0·36570	0·37492
1·65	0·64453		2·45	0·32469	
1·70	0·68483	0·68471	2·50	0·27470 estim.	
1·75	0·71534		2·55	0·23797	
1·80	0·73565	0·73597	2·60	0·19277	0·19381
1·85	0·74487		2·65	0·15598	
1·90	0·74459	0·74637	2·70	0·12393	0·12548
1·95	0·73394		2·75	0·09593	
2·00	0·71395	0·71624	2·80	0·07304	0·07804
2·05	0·68587		2·85	0·05144	
2·10	0·65083	0·65441	2·90	0·03443	0·03533
2·15	0·60995		2·95	0·02046	
2·20	0·56479	0·56967	3·00	0·00922	0·01002
2·25	0·51647				

This comparison is made in Table XI.

We also have that

$$x_0(i) = 0{\cdot}25\frac{x_0(2{\cdot}5)}{x_p(2{\cdot}5)} = 0{\cdot}068436$$

and that

$$(RD)_{\text{calc.}} = 1{\cdot}11388$$

Finally, $D = 0{\cdot}4583$, and therefore,

$$R_{\text{min.}} = 2{\cdot}420$$

It is seen then from Table XI that again on the whole, the agreement between $\lambda\, Dx_0(\lambda)$

Table XII. Some numerical values of the Riemann zeta function.

i	$\zeta(2i)$
1	1·644934
2	1·082323
3	1·017343
4	1·004077
5	1·000995
6	1·000246
7	1·000061
8	1·000015
9	1·000004

will adequately illustrate the semi-continuous problem; because the problem with more distinguishable components would, in principle at least, be essentially identical to the one just discussed. Table XII gives some numerical values for the Riemann zeta function.

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Dimensional systems and systems of units in physics with special reference to chemical engineering

Part II. Practical rules for authors and readers and the need for their observance

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(*Received* 23 *January* 1955)

1. INTRODUCTION AND SUMMARY

In Part I the principles were discussed of constructing systems of units. The results of this study will now be applied to formulate a number of practical rules, the application of which should reduce the amount of misunderstanding in the field.

Most of these rules are intended for authors (see § 2). The main line of thought therein refers to the case where an equation in physics or engineering is derived from first principles and then numerically applied (rules 1-9).

Separate statements are given with reference to

empirical equations (rule 10),
dimensional analysis (rule 11),
dimensionless groups (rule 12),
equations that should be applicable in more than one dimensional system (rule 13).

In § 3 a few recommendations are given for the use of the readers.

In § 4 a number of literature quotations are analysed. This discussion shows that many authors put problems before the readers, which, it is suggested, they could have avoided.

Finally, a summary is presented of advantages and disadvantages of various systems, either derived by *a priori* considerations or from the analysis of the literature.

The weighing of these arguments is of course a subjective procedure. It is considered that following systems are preferable :

Metric : the practical system (m, kg (mass), sec., °C, practical electrical units),

British : the lb (mass), lb (force), ft., sec., BTU, °F system.

2. PRACTICAL RULES FOR THE AUTHOR

1. *The advice is given to consider letter symbols to stand for physical magnitudes and not for their numerical values only.*

This means that statements like : " the acceleration by gravity is g m/sec.^{2} " are not allowed.

2. *Decide on a coherent set of fundamental quantities and dimensional constants and use it consistently.*

The sets of quantities discussed in Part I are :

In mechanics :

(*a*) MLT* : dynamic systems.
(*b*) FLT : static systems.
(*c*) FMLT : English engineering system.

In mechanics + heat :

(*d*) MLTQθ, e.g.: cgs system : g_m, cm, sec., cal., °C. Brit. dyn. system : $lb._m$, ft., sec., BTU, °F.
(*e*) MLTθ, e.g.: pract. system : kg_m, m, sec., °C.
(*f*) FLTQθ, e.g.: kg_f, m, sec., kcal., °C. $lb._f$, ft., sec., BTU, °F.
(*g*) FMLTQθ, e.g.: $lb._f$, $lb._m$, ft., sec., BTU, °F.

In mechanics + heat + electricity :

(*h*) MLTQθ, the cgs system : g_m, cm, sec., cal., °C.
(*i*) MLTθI, the practical system : kg_m, m, sec., °C, ampère.

The above list represents a choice of the most important combinations of wide applicability. Others, such as practical electrical units + mechanical cgs units, are also met.

* M = Mass, L = Length, T = Time, F = Force, Q = Heat, θ = Temperature, I = Electric current.

Excluding applications of Newton's First Law (mutual attraction of masses), the dimensional constants to be used with the above sets of quantities are :

In mechanics :

(*a*) none.

(*b*) none.

(*c*) $g_c = \left[\frac{\mathrm{ML}}{\mathrm{FT^2}}\right]$ { in $\mathrm{lb._f\,lb._m\,ft.\,sec.}$ system : $g_c = 32{\cdot}2\ \frac{\mathrm{lb._m\,ft.}}{\mathrm{lb._f\,sec.^2}}$; in $\mathrm{lb._f\,lb._m\,ft.\,hr.}$ system : $g_c = 4{\cdot}17 \times 10^8\ \frac{\mathrm{lb._m\,ft.}}{\mathrm{lb._f\,sec.^2}}$ }

In mechanics + heat :

(*d*) $J = \left[\frac{\mathrm{ML^2\,T^{-2}}}{\mathrm{Q}}\right]$ = mech. equivalent of heat

in cgs system : $J = 4{\cdot}19 \times 10^7\ \frac{\mathrm{erg}}{\mathrm{cal}}$

in Brit. dyn. system : $J = 24{\cdot}1\ \frac{\mathrm{ft.\ poundal}}{\mathrm{BTU}}$

(*e*) none.

(*f*) $J = \left[\frac{\mathrm{FL}}{\mathrm{Q}}\right]$, in techn. metric system : $J = 427\ \frac{\mathrm{kg_f\,m}}{\mathrm{kcal}}$

in $\mathrm{lb._f}$ ft. sec. BTU. °F system : $J = 778\ \frac{\mathrm{lb._f\,ft.}}{\mathrm{BTU}}$

(*g*) $g_c = \left[\frac{\mathrm{ML}}{\mathrm{FT^2}}\right]$, as under (*c*).

$J = \left[\frac{\mathrm{FL}}{\mathrm{Q}}\right]$, in $\mathrm{lb._f\,lb._m}$ ft. sec. BTU. °F — system : $J = 778\ \frac{\mathrm{lb._f\,ft.}}{\mathrm{BTU}}$

In mechanics + heat + electricity :

(*h*) one dimensional constant in some formulae in electricity and magnetism.

(*i*) μ_0 = permeability of vacuum = $\frac{4\pi}{10^7}\ \frac{\mathrm{V\,sec.}}{\mathrm{A\,m}}$

ϵ_0 = dielectric constant of vacuum = $= \frac{10^7}{4\pi(3 \times 10^8)^2}\ \frac{\mathrm{A\,sec.}}{\mathrm{V\,m}} = 8{\cdot}854 \times 10^{-12}\ \frac{\mathrm{A\,sec.}}{\mathrm{V\,m}}$

Examples A 11 and A 12 in § 4 show difficulties that arise through unsystematic use of dimensional systems.

3. *Decide on factors fixing numerical constants.*

Some of the alternatives have been mentioned in Part I, e.g. :

rationalization or non-rationalization in the field of electricity and magnetism ;

various ways of defining a Reynolds group (radius vs. diameter of pipe ; particle size vs. inverse of specific particle surface) ;

various ways of defining the friction factor for flow through a pipe (the American : f = shear stress at wall divided by $\frac{1}{2}\rho v^2$, the European : $\lambda = 4f$ = pressure drop divided by $\frac{1}{2}\rho v^2 \cdot \frac{l}{d}$).

Deviations from accepted custom in this respect cannot be traced by dimensional checks.

It is impossible to give precise instructions. Rule 3 only serves as a reminder that in deriving physical relationships a number of conventions are used, often unconsciously.

4. *Prepare a list of quantities and dimensional constants giving their symbols, names and dimensional formulae, and keep this list complete.*

5. *Write down equations in letter form, ensuring dimensional homogeneity by using appropriate dimensional constants. Carry out the necessary mathematical transformations and check dimensional homogeneity of the final result.*

Remark—The final check is in principle superfluous but it is very useful to help in detecting mistakes.

6. *With equations in letter form, do not prescribe the units to be used when this constitutes an unnecessary limitation.*

7. *Choose a unit for each fundamental quantity. Substitute the units in the dimensional formulae for the derived quantities in order to obtain the units of these derived quantities.*

8. *In order to prepare the equation for numerical use, replace constants* (dimensional constants, physical quantities that happen to be constant in the given problem) *by their numerical values. From this point onward, mention each time the units to be used.*

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It is convenient to mention the unit of the numerical factor in order that users of the equation may easily convert it into their own system.

THORNE and WALSHAW in their booklet " Engineering Units and the Stroud Convention " (1954) give prescriptions how to derive numerical equations from physical equations.

Their physical equations, which cover the fields of mechanics and heat are always written without the dimensional constants, g_c and J. This is how they come to the statement (p. 2) that physical equations are completely free from any restrictions as regards particular units or systems of units (see, however, Part I, page 132).

In a dimensionally homogeneous physical equation THORNE and WALSHAW then replace the letter symbols by products of numerics and units. No prescription to use a coherent system of units is given so that the resultant equation is " unitarily inhomogeneous." By inspection the so-called " unity brackets " are then chosen and added as extra factors (each being unity) to obtain unitary homogeneity. These factors cover :

the conversion of size of unit :

$$\text{e.g.: } \left[\frac{5^\circ\text{C}}{9^\circ\text{F}}\right]; \left[\frac{3600 \text{ sec.}}{1 \text{ hr.}}\right]$$

the replacement of derived units by fundamental units :

$$\text{e.g. : } \left[\frac{\text{dyne sec.}^2}{\text{g cm}}\right]; \left[\frac{\text{lb.}_f \text{ sec.}^2}{\text{slug ft.}}\right]$$

the change in fundamental unit :

$$\text{e.g. : } \left[\frac{32{\cdot}2 \text{ lb.}_m \text{ ft.}}{\text{lb.}_f \text{ sec.}^2}\right]; \left[\frac{778 \text{ ft. lb.}_f}{\text{BTU}}\right]; \left[\frac{\text{knot hr.}}{6080 \text{ ft.}}\right]$$

This subdivision of " unity brackets " in three groups has been mentioned here for the purpose of seeing the relations with the present article. It is, however, artificial and we may just as well say that by not having systems of units, THORNE and WALSHAW leave the equations in physics full of " dimensional constants," which they do not write in equations in letter form and must introduce later.

9. *Give the list sub 4 at the end of the article. If desired the dimensional formulae can be replaced by the units.*

Remarks—1. Obviously, such a list cannot allow alternatives.

2. In expressing the units it is not necessary to use fundamental units only. It may be more convenient to use some very important derived units, such as : dyne, erg, newton, joule, or, volt. They have precisely been given their names for that that purpose.

10. *Empirical equations that are not dimensionally homogeneous, should never be given without stating the units of the various letter factors.* Preferably the unit of any dimensional numerical factor should be mentioned in order to facilitate conversion.

11. *Dimensional analysis need not be carried out with the fundamental units the author uses generally.* There is an advantage in using the maximum number of fundamental units compatible with the problem. No unnecessary dimensional constants must be included in the set of quantities to which dimensional analysis is applied.

Remarks—1. In heat transfer without conversion of heat in mechanical energy or vice versa, heat will be given a separate dimension – even if practical units are used elsewhere – without, however, introducing the mechanical equivalent of heat.

2. A statement by GUGGENHEIM [1] is highly appropriate :

> ". . . the number of fundamental quantities having independent dimensions is, to some extent, a matter of choice. But, if in the same problem or set of problems two authors make a different choice, the one choosing the greater number is likely to be the more competent physicist."

12. *Use dimensionless groups to the utmost.*

All complete equations can be written as relations between dimensionless groups.

There is an advantage, in giving data and in presenting relationships in analytical or graphical form to use dimensionless groups to the greatest possible extent, since :

1. The numerical values of dimensionless groups are independent of the choice of the system of dimensions and the further choice of the sizes of the units ;
2. The number of variables is reduced thereby, so that equations assume their simplest form and the amount of experimentation to derive an empirical relationship is a minimum.

It is advantageous to introduce dimensionless groups at an early stage of the mathematical transformation, for instance to write already the governing differential equation and boundary conditions in dimensionless form.

In calculating numerical values of dimensionless groups coherent units must be used. Thus, if each symbol for a physical magnitude is replaced by the product of a numerical value and a unit, expressed in fundamental units, all units cancel.

Examples B 5 and 7-13 signal cases where the units as prescribed are inconsistent and yet the correct result is given. Thus, the author did not follow his own prescription.

In Examples B 1 and 6 the units are not coherent and the result deviates from the generally accepted one.

13. *Multi-purpose formulae.*

If formulae are to be ready for use with more than one system of units, following rules apply :

(*a*) If all systems of units, in the field covered by the calculations, require the same numerical factors and dimensional constants, the equations in letter form are valid for all of them.

(*b*) If numerical factors and/or dimensional constants differ, the equations should be provided with factors and constants for all cases, with precise instructions where to drop those.

The survey by KRONIG [2] of equations for rationalized practical units and for various types of cgs electrical units is given in this manner.

The combination of a dynamical system with the English Engineering system would require the introduction of g_c with the instruction to drop it for the dynamical systems. Failure to do so cannot be corrected by conversion of units (vide example A 8).

3. PRACTICAL RULES FOR THE READER

1. *Check on observance of rules by author.*

2. *If desired, convert equations in letter form to the own preferred system by following methods :*

(*a*) If the set of dimensional constants in the reader's preferred system is comprised in the set used by author :

Omit any superfluous dimensional constants.

Example :

Author : $g_c F = ma$ (Engl. Engineering).

Reader : $F = ma$ (static and dynamic systems).

(*b*) If the reader's set contains new dimensional constants :

Find by a dimensional check which dimensional constants are to be included.

Example :

Author : $pV = RT$ (practical system).

$p = [\mathrm{ML^{-1}\,T^{-2}}]$.

$V = [\mathrm{L^3\,Mol^{-1}}]$.

$R = [\mathrm{ML^2\,T^{-2}\,Mol^{-1}}\ \Theta^{-1}]$

$T = [\Theta]$.

Reader : $pV = JRT$ (cgs system + cal + °K).

$p = [\mathrm{ML^{-1}\,T^{-2}}]$.

$V = [\mathrm{L^3\,Mol^{-1}}]$.

$R = [\mathrm{QMol^{-1}}\ \Theta^{-1}]$.

$T = [\Theta]$.

so that : $J = [\mathrm{ML^2\,T^{-2}\,Q^{-1}}]$.

Remark—Caution is necessary in the fields of electricity and magnetism in converting cgs into practical units and vice versa. Equations may differ by a numerical factor 4π, due to the fact that the practical system is rationalized and the cgs system is as a rule not. In cases of doubt, it is recommended to consult tables.

3. *Conversion of units of physical quantities and constants in numerical equations.*

(a) *Conversion within the same dimensional system.*

If each quantity is considered to be the product of a numerical factor and a unit the conversion is easily carried out with the aid of the conversion factors for the fundamental units.

One method is, simply to replace each fundamental unit from one system by its equivalent in the other. Thus, for example,

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100 lbs./cu.ft. =
$= 100 \times 0{\cdot}454 \text{ kg}/(0{\cdot}3048 \text{ m})^3 = 1602 \text{ kg/m}^3$

If a ready conversion factor is used, it may be applied in the wrong direction unless one uses the principle adopted by VAN DIJCK [3] of heading tables in the following manner :

Quantity	*Expressed in*	*→ to multiply with → ← to divide by ←*	*Expressed in*
force	dyne	10^{-5}	newton

(b) *Conversion to another dimensional system.*

It is probably safer not to attempt to convert to units of other dimensional systems but to change the dimensional system already in the equation in letter symbols, as mentioned in para. 2.

Example A 8 indicates the sort of difficulties one might otherwise encounter.

4. EXAMPLES

In most cases the authors make no numerical mistakes. Yet their prescriptions, if duly carried out, would often lead one to do so.

It is the aim of the following discussion to prove that insufficient attention in this respect places an extra burden on the reader.

The examples are grouped under the following headings :

A. Unsystematic use of dimensional formulae and dimensional constants and incorrect statements thereon.

B. Inconsistencies in the substitution of numerical values in equations.

Regarding subject B, the substitution of numerical values in equations, it is noted that the author may :

1. give an incomplete description of the units to be used in his equations ;
2. give an overcomplete description, i.e. leave alternatives to choose from ;
3. describe an inconsistent set of units.

   In this respect it is most dangerous to omit a dimensional constant from a coherent set, when the incoherence easily escapes attention ;
4. describe no units at all.

   This is in many cases acceptable, viz. when no numerical application is given, when it is clear what dimensional system has been used and it is left to the reader to choose the sizes of the fundamental units.

A. *Unsystematic use of dimensional formulae and dimensional constants, incorrect statements on dimensional systems.*

A 1. Author A 1* under a heading " cgs system " mentions erroneously :

conversion factor $g_c = 980{\cdot}6 \dfrac{g_m \text{ cm}}{g_f \text{ sec.}^2}$

unit for the gas constant R : $\dfrac{g_f \text{ cm}}{\text{mol } ^\circ\text{C}}$

In a column " English " analogous definitions are given together with a statement that the unit of force is the poundal. However, lb._f and poundal are incompatible.

Elsewhere g_c is incorrectly given as 32·17 $(\text{lb.}_m/\text{lb.}_f)/(\text{ft./sec.})$.

A 2. Authors A 2 in their notation use F, M, L, T, Q and Θ as fundamental quantities and give corresponding dimensional formulae, such as pressure drop $[FL^{-2}]$ and density $= [ML^{-3}]$. This is the English Engineering system, new version.

The text, however, equates a pressure drop to a density times a length, which means that F and M have been equated, as described on page 136, Part I (English Engineering system, old version.)

A 3 and 4. At one place the author of A 3 presents an admirable treatise on the use of the English Engineering system (new version) with the dimensional constant g_c. At other places there are some misstatements regarding the unit in which this constant is expressed, viz.:

A 3, elsewhere, $g_c = 4{\cdot}18 \times 10^8$ lb force × ft./(pounds fluid) (hr.) (hr.)

A 4, same author, $g_c = 4{\cdot}17 \times 10^8 \dfrac{\text{lb matter ft.}}{\text{hr.}^2}$

A 5. The authors of A 5 make no distinct

* The list of authors has been submitted to the Editor of this Journal but will not be published.

choice between the three systems mentioned in § 2, rule 2, a, b, and c, having

	fundamental units	*derived units*
(*a*)	$lb._m$, ft., sec.	poundal
(*b*)	$lb._f$, ft., sec.	slug
(*c*)	$lb._m$, $lb._f$, ft., sec.	—

They define four fundamental dimensions (system (*c*)) but use the units sub. (*b*) for them, one of which is a derived one. Newton's Law is then used to derive a relation between the fundamental dimensions (logically impossible!) in order to decrease their number to three (system (*a*) or (*b*)).

The notation is unsystematic, e.g.

power	ft.lb./sec.	occurs in system	(*b*) and (*c*)
density	slug/cu.ft. or	,, ,, ,,	(*b*) or
	$lb._m$/cu.ft.		(*a*) and (*c*)
viscosity	$lb._m$/ft.sec.	,, ,, ,,	(*a*) and (*c*)
force	$lb._f$	,, ,, ,,	(*b*) and (*c*)
mass	slug	,, ,, ,,	(*b*)

A 6. Author A 6 defines a permeability K_1 of a porous bed measuring pressure in g/cm²; viscosity in poises, length in cm and linear velocity in cm/sec. Thus the quantity defined is the product of the permeability in cm² (usual definition) and the dimensional constant g in cm/sec.²

As a result of the above, an equation is obtained relating permeability to porosity (dimensionless) and specific surface S_0 (cm^{-1}) of following form :

$$K_1 = \frac{g\,\epsilon^3}{5\,S_0^2\,(1-\epsilon)^2}$$

where g makes a mysterious appearance.

The List of Symbols says that all units are consistent cgs units except where otherwise stated. It omits to give a unit for K_1, and this is definitely not a cgs unit.

A 7. Authors A 7 give author's A 6 equation in the following form :

$$S_0 = 14\sqrt{\frac{\epsilon^3}{K_1(1-\epsilon)^2}}$$

Commenting thereon, in this equation the factor 14 is a dimensional constant $\left(\sqrt{\frac{g}{5}}\right)$. Again the dimension of K_1 is omitted in the Notation. The equation in which K_1 is defined is not of much avail, since the prescription is given to insert the viscosity in centipoises instead of poises.

A 8. Authors A 8 use formulae valid in dynamical systems, i.e. not including g_c. They wanted to make the result applicable with the English Engineering system (using hours) as well, by indicating conversion factors in the list of symbols.

The pressure drop in N/m^2 then has to be replaced by g_c times the pressure drop in lb_f/sq.ft. To say Δp = pressure drop N/m^2 ($= 8{\cdot}7 \times 10^6$ lb. force/ft.²) is incorrect.

A 9. Author A 9 gives in one article formulae valid for the metric equivalent of the English Engineering system (old version), involving a dimensional constant g (in cm.sec.$^{-2}$), and formulae valid for the cgs system. The Table of Symbols says that pressure is expressed in cm water gauge or g cm^{-2}, which is incompatible with the cgs formulae.

A 10. Authors A 10 have expressed the pressure difference over a pipe section, Δp, in static units (lb/sq.ft.) and the shearing stress F at the wall of the pipe in dynamic units (lb/ft.hr.²) in accordance with their list of symbols. When using the English Engineering system a choice must be made, as mentioned in Part I (page 136) whether quantities are expressed in the one way or the other. It is very unfortunate that in defining the units for two so closely related quantities as a normal and a tangential force per unit area, different routes have been used.

Consequently the equation relating Δp, F and the pipe dimensions (d and l) contains g as a dimensional constant, viz.:

$$\Delta p \,.\, \frac{\pi d^2}{4} = \frac{F}{g} \,.\, \pi\, l\, d$$

with $g = 4{\cdot}18 \times 10^8$ ft./hr.²

However, later on, again for pressure drop along a pipe, eq. (41) reads

$$p_1 - p_2 = \frac{4l}{d} F \text{ (note absence of } g)$$

Here the context shows that pressure is expressed in the dynamic unit lb./ft.hr.²

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A 11. Author A 11 in discussing the fine-structure constant $\frac{ch}{2\pi e^2}$ (c = velocity of light, h = Planck's constant, e = charge of electron) says: "it is frequently referred to as "dimensionless," for example when EDDINGTON states that when we say that its value is 137 "we are eliminating all reference to our artificial standards." It is clear, however, that this is not so."

We should like to say that the fine-structure constant, being the ratio of two like quantities (the velocity of light and the velocity of the electron in the first orbit in a hydrogen atom) is truly dimensionless so that its value is independent of our standards.

It is only the expression for it that does depend on our standards $\left(\text{electrostatic cgs system}: \frac{ch}{2\pi e^2}, \right.$ practical system: $\left. \frac{2ch\epsilon_0}{e^2}\right)$.

The fact that the fine-structure constant is dimensionless should not be checked by substituting in the e.s. cgs definitional equation the dimensional formulae for the various quantities from another system, involving an ϵ_0, as it has been done.

A 12. An interesting paradox is mentioned by POHL [4].

Any charge can be expressed in e.s. cgs units or in e.m. cgs units and it is therefore possible to equate the two, to give e.g.

$$1 \text{ e.m. cgs unit of charge} = 3 \times 10^{10} \text{ e.s. cgs units of charge} \quad (1)$$

Now the e.m. unit and the e.s. unit are related to fundamental units as follows:

$$1 \text{ e.m. cgs unit of charge} = 1 \text{ cm}^{1/2}\,\text{g}^{1/2} \quad (2)$$

$$1 \text{ e.s. cgs unit of charge} = 1 \text{ cm}^{3/2}\,\text{g}^{1/2}\,\text{sec}^{-1} \quad (3)$$

Inserting (2) and (3) in (1) gives:

$$1 \text{ sec.} = 3 \times 10^{10} \text{ cm} \quad (4)$$

VERMEULEN [5] says the cause is to be sought in the essentially different symbolic nature of these products.

Following statement elaborates hereon: Eq. (2) holds within the dimensional system used in forming e.m. units and *within* that system the product formations and so on can be regarded as normal mathematical routine.

Eq. (3) similarly holds within the dimensional system used in forming e.s. units.

In view of these restrictions the eq. (2) and (3) are in general incompatible and cannot be combined to give eq. (4).

The e.s. and e.m. systems would become identical if such units of length and time were used that the velocity of light, $c = 1$ (see Part I, page 134). This is precisely what is found in eq. (4).

A 13. Authors A 13 say that the diameter D_b of bubbles formed in boiling is proportional to

$$\sqrt{\frac{2\,g_0\,\sigma}{g\,(\rho_l - \rho_v)}}$$

and their list of symbols says:

D_b = diameter of bubble, ft.
g = acceleration of gravity.
g_0 = conversion factor
σ = surface tension, dynes/cm or lb./ft.
ρ_l, ρ_v = densities of liquid and vapour, lb./cu.ft.

If lb._m and lb._f are not distinguished, g and g_0 are identical.

B. *Inconsistencies in the substitution of numerical values in equations.*

B 1. Authors B 1 in studying the resistance of pipes calculate a group $\frac{\Delta P}{\rho u^2}\,\frac{D}{L}$ and plot it against a Reynolds number.

The units for ΔP and ρ being derived from lb_f and lb_m respectively the above group should have been made dimensionless by including a factor $g_c = 32{\cdot}2\,\frac{\text{lb.}_m\,\text{ft.}}{\text{lb.}_f\,\text{sec.}^2}$.

The "friction factor" – Re graph as given, accordingly differs from those obtained by a consequent application of coherent units.

See also example B 6.

B 2. Authors B 2 define the coefficient of friction ψ for the turbulent flow of an incompressible fluid in a smooth pipe by

$$p_1 - p_2 = \psi \frac{l}{d} \cdot \tfrac{1}{2} \rho w^2$$

with $p_1 - p_2$ = pressure drop (in cm water) over the length l (in cm)
d = diameter in cm
w = mean velocity in cm/sec.
ρ = density in g/cm^3
ψ = dimensionless.

With the other units as prescribed, $p_1 - p_2$ should have been expressed in dynes/cm^2 = g cm^{-1} sec.$^{-2}$. The ratio between a pressure difference and a liquid head is ρg, i.e. for water, 981.

B 3. Authors B 3 describe the addivity of resistances in mass transfer between phases. With the units given, k_L is in cm/hr. and the product of the Henry coefficient with K_G is in litre/hr. cm^2.

B 4. Authors B 4 give the following equation for the heat transport through a very dilute gas between parallel walls at temperatures T_1 and T_2:

$$Q = \frac{3}{8} p \sqrt{\frac{3R}{MT}} (T_1 - T_2)$$

where : p = pressure
T = average temperature
M = molecular weight
R = gas constant.

Q is not defined but the general list of symbols says : Q = quantity of heat, with dimension : kcal.

The Q in the above equation represents heat per area time but Q and R can only be expressed in mechanical units.

B 5. Author B 5 gives for water at 100°C :

specific heat

$c_p = 1{\cdot}011$ kcal kg^{-1} °C^{-1}

viscosity

$\mu = 8{\cdot}0 \times 10^{-9}$ kg hr. m^{-2} (i.e. kg$_f$ hr. m^{-2})

thermal conductivity

$k = 0{\cdot}588$ kcal hr.$^{-1}$ m^{-1} °C^{-1}

and N_{Pr} (i.e. Prandtl group)

$= 1{\cdot}75$ (dimensionless).

The Prandtl group had been previously defined as $\frac{\mu c_p}{k}$. The above data would give $\frac{\mu c_p}{k} = \frac{1{\cdot}75}{1{\cdot}80 \times 10^5} \frac{\text{kg m}}{\text{kg}_f \text{ hr.}^2}$. It is immaterial whether the c_p is thought to be referred to kg$_f$ or kg$_m$, the difference being that the forgotten multiplier is to be interpreted as g or g_c.

In order to arrive at the correct result : either the dimensional system should be adjusted to the units by the inclusion of the dimensional constant g or g_c, or the units adjusted to a dynamical dimensional system by expressing μ in kg$_m$ m^{-1} hr.$^{-1}$

Remark—This case is closely related to B 11 and B 12.

B 6. Author B 6 defines the Reynolds group by

$$Re = \frac{Dus}{z}$$

where : D = diameter of pipe (inches)
u = velocity (ft./sec.)
s = specific gravity referred to water at 60°F (dimensionless)
z = absolute viscosity in centipoises.

The value differs from the usual one by a factor $\frac{1}{7740}$. The friction factor versus Re graph changes accordingly.

It is felt that by this procedure the great advantage of dimensionless groups, their universality, is lost.

B 7 and B 8. Authors B 7 and author B 8 prescribe to express diameter in ft., velocity in ft./sec., density in lb./cu.ft. and viscosity in lb./sec.hr. The Reynolds group thus calculated would be a factor 3600 low.

B 9. Authors B 9 = B 7 in their Notation prescribe noncoherent units, e.g. :

particle diameter	D_p, mm
gas velocity	U, ft.sec.$^{-1}$
density	ρ, g.cm^{-3}
viscosity,	μ, centipoise
diffusivity	D_v, sq.ft. hr.$^{-1}$

These cannot have served in calculating the dimensionless groups $Re = \frac{D_p U \rho}{\mu}$ and $Sc = \frac{\mu}{\rho D_v}$, the numerical values of which are given correctly.

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B 10. Authors B 10 in their Notation leave alternative choices, viz. diffusivity D in sq.cm/sec. or sq.cm/day; viscosity μ in centipoises or lb./sec.ft. The density ρ is expressed in lb./cu.ft.

It is also impossible to select a coherent set of data to substitute in $\frac{\mu}{\rho D}$ = the Schmidt group.

B 11. Author B 11 defines $Pr = \frac{\nu}{a} \left(= \frac{\eta c_p}{\lambda}\right)$ and gives following data in his tables:

c_p = in kcal/kg °C
η = in kg sec./m^2
λ = in kcal/m hr. °C
Pr = dimensionless

However, with these units $\frac{\eta c_p}{\lambda}$ is expressed in $\frac{\text{hr. sec.}}{\text{m.}}$ and the multiplication with $3600 \frac{\text{sec.}}{\text{hr.}} \times 9{\cdot}81 \frac{\text{m}}{\text{sec.}^2}$ is left to the reader.

B 12. Author B 12 does the same as author B 11.

B 13. Author B 13 defines $Pr = \frac{c_p \mu}{k}$ with the following units:

c_p in BTU/lb. mole °F
μ in lb./sec.ft.
k in BTU/hr. ft. °F

Note inconsistencies: lb. mole and lb., hr. and sec.

The *Sc* group cannot be calculated either.

5. The Suitability of Various Systems of Units to the Chemical Engineer

In this section we shall:

A. Enumerate the properties, desirable in a system of units;

B. Discuss these desiderata and examine in how far they can be reached;

C. Compare various systems.

A. *Desiderata*

For convenience and clarity the following is considered desirable:

General requirements

1. To use a coherent system of units in the particular field in which the chemical engineer is working.
2. To let such a coherent system of units cover at least the fields of mechanics and heat.
3. To strive to a one-to-one correspondence between the quantities and their units and/or dimensional formulae, i.e.
   - 3*a*. Each quantity should have a single dimensional formula and unit.
   - 3*b*. Each dimensional formula and unit should correspond to a single quantity only (see FLEISCHMANN [7]).
   - 3*c*. As a logical consequence of 3*b* physical quantities should not be dimensionless.
4. To use a small number of dimensional constants.
5. To employ such dimensional formulae and to express the derived units in such a manner that clarity is best served. This means that it should be obvious how the chosen expression is related to a definitional equation for the quantity under consideration. In this way it is easiest to remember the unit for the given quantity and vice versa.
6. To choose such a system that the acceleration by gravity appears only when gravity actually plays a role.

Specific requirements re units

7. Units should be well defined.
8. Use *must* be made of following units:

	metric	*British*
length	m or cm	ft.
mass and/or force	kg or g	lb.
time	sec.	sec. or hr.
temperature	°C	°F or °C

9. Due consideration must be given to the systems used by physicists, mechanical engineers and electrical engineers, since their equations and data will be used.

B. *Discussion of desiderata*

1. *Coherent units*

A great majority of physicists and engineers use a coherent system of units. If their basic data

are given in other units, they carry out the conversions before substituting them in the equations.

It should however, be placed on record that it is not necessary to do so (see discussion on THORNE and WALSHAW's method, Part II, page 169).

2. *Width of field*

Special systems are sometimes used in a restricted field. Permeability of porous media, for instance, is expressed in darcy's. We might say that there is an "atm./cm ; cm/sec. ; centipoise ; darcy system " for the use in Darcy's Law only.

As long as this is only applied in this particular field it works satisfactorily. If, however, permeability is related to particle size, shape and porosity it becomes more practical to express it in m^2 or cm^2.

Likewise, in heat transfer there is a preference for hours, in other fields for seconds. Inconsistencies in the use of seconds and hours become apparent in examples B 7-8-9-11-12 and 13. It is considered that a consistent system for mechanics and heat is to be preferred and that it should be based on the second.

The various static, dynamic and engineering systems, amplified with a unit of temperature and in some cases with a heat unit, as discussed, all fulfil this requirement.

In the following it is taken for granted that such a coherent system will be used.

3. *"One-to-one" correspondence*, and

4. *Small number of dimensional constants*

Rule 3*a* asks for a large number of dimensional constants ; a compromise with rule 4 must thus be found.

Notable violations of 3*a* are :

cgs system applied to electricity and magnetism, giving two sets of units ;

English Engineering system (old and new), giving alternative choices for various units.

Notable violations of 3*b* are that the same unit is employed

in	*for*
cgs e.s. system	electric capacity and length
cgs e.m. system	inductance and length
English Engin. system, old version	force and mass

Notable violations of 3*c* are :

cgs e.s. system	dielectric constant
cgs e.m. system	magnetic permeability
heat units described in Part I, p. 138–9, ad 3	specific heat, specific entropy

The necessity to use a small number of dimensional constants can be underlined by reference to frequent conversions requiring the mechanical equivalents of heat and electrical energy and to a considerable amount of misunderstanding about the conversion factor g_c (Par. 4, Ex. A 1, 3, 4, 13).

The practical system of course introduces μ_0 and ϵ_0 but avoids the conversion from practical electrical units to cgs units and back.

Further refinement in the sense of requirement 3 would be possible by distinguishing the three length co-ordinates in dimensional analysis and in units, or perhaps by introducing vector concepts. This is considered too complicated for general use, i.e. it is considered inevitable that torque and work have the same unit and that an angle (= arc/radius) will be dimensionless.

5. *Clarity of dimensional formulae*

Regarding clarity of dimensional formulae it is essential to introduce one new fundamental unit when entering a new field of physics, i.e.:

temperature in the field of heat (all systems discussed, see Part I, p. 138) ;

one electrical unit in the field of electricity and magnetism (practical system, see Part I, p. 139).

This is contrary to the principle of making so-called absolute units, based on mechanics alone, which for a long time has been the ultimate aim of physicists.

Requirements 3 and 5 are closely related, both acting contrarily to No. 4.

6. *The place of "g" in equations*

Requirement 6 disallows static systems (for the

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reason explained in Part I, pp. 137-8) and the old version of the English Engineering system (Part I, p. 136).

7. *Definitions of units*

In order to properly define a unit of force, with the aid of a standard kilogram, or pound, it is necessary to specify a standard acceleration of gravity ($g = 980{\cdot}665$ cm/sec.^{2} at 45° latitude at sea level). Consequently the force of gravity acting on 1 $lb._m$ elsewhere in general is *not* 1 $lb._f$. This reduces the supposed simplicity of static systems.

8. *Use of existing units*

All systems discussed in this paper conform to this requirement.

9. *Units used in physics and various branches of engineering*

In general physicists prefer dynamic systems and mechanical engineers static systems.

Static systems have the advantage of having well understood units for force, pressure, etc. (derived from kg_f, g_f, $lb._f$) but the disadvantage of not having suitable mass units. This condemns them for use in general physics.

Dynamic systems have suitable mass units but the unit of force (newton, dyne, poundal) is considered less suited by mechanical engineers.

The English Engineering system allows conventional units for both force and mass, however, at the expense of conformity to requirement 3*a*.

C. *Comparison of systems*

It is considered that the English Engineering system (new version) has more advantages than disadvantages when compared to static systems and to the English Engineering system (old version).

Hence the choice is one between the English Engineering system (new version) – or its metric equivalent – and dynamic systems.

It should be noted that E. SCHMIDT declares himself in favour of a kg_f, kg_m, m, sec. system but does not use it since there is no further literature in it.

The comparison between engineering systems (new version) and dynamic systems is different for British and metric units.

In British units the argument to be in line with physics does not count so much, much of the physical data being in metric units. The entire field of electricity is in the metric system. Therefore the English Engineering system may be a very suitable compromise to satisfy the mechanical engineers.

Its disadvantages were noted to be the following:

1. Alternative possibilities of defining dimensions of physical quantities with consequent alternatives where to place the dimensional constant g_c.
2. Difficulty to grasp the significance of g_c.

A variety of false statements have been found (examples A 2, 3 and 4).

It is necessary that the pounds (mass and force) are well distinguished. Simplest, but not self-evident, are lb. and Lb. [6]. In this paper, lb_m and lb_f have been used. The abbreviations lb (mass) and lb (force) are also employed.

In metric units contact with physics counts much more. Here a dynamical system is considered to be at its place. The choice between cgs and practical units in physics is largely governed by the fact that practical units are indispensable in electricity and signs are that cgs units will be completely abolished in this field. There is accordingly a strong current to do the same through all physics. Hence it is considered that the metric chemical engineer should use the practical system.

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Mixing by agitation of miscible liquids

Part I.

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(*Received* 9 *July* 1954)

Summary—The performance of several types of agitators has been studied for the mixing of miscible liquids in batch operation.

The time was measured necessary to homogenize two super-imposed layers of miscible liquids. An optical technique, known as the " Schlieren " method, was used to determine the moment at which uniformity is reached. In addition, the power consumption of the stirrers was measured. The influence of liquid properties and of the conditions of agitation was ascertained and could be explained.

The results enabled relations containing dimensionless groups to be derived for both mixing time and power consumption.

An important result of this study is the discovery that in the region of turbulent flow the mixing time is related to the pumping capacity of the stirrer. The mixing time appears to be approximately proportional to the time required to circulate the liquid once, this time being equal to the ratio of the liquid volume to the pumping capacity of the stirrer.

General rules for the optimum shape and dimensions of the stirrers were established from the relations derived for mixing time and power consumption.

A few experiments were carried out on steady-state mixing (continuous mixing) of liquids, the results of which were in agreement with those of the batch experiments.

Résumé—L'auteur étudie l'efficacité de nombreux types d'agitateurs pour le mélange de liquides miscibles dans une opération discontinue. Il mesure le temps nécessaire à homogénéiser les deux couches superposées. Il utilise une technique optique, connue comme méthode de " Schlieren," pour déterminer le moment où l'homogénéité est atteinte. Il mesure aussi la consommation en puissance des agitateurs. Il établit et peut expliquer l'influence des propriétés du liquide et des conditions d'agitation.

Les résultats permettent d'établir des relations, impliquant des groupes sans dimension à la fois pour le temps de mélange et la puissance consommée.

Cette étude apporte un résultat important : dans la région d'écoulement turbulent, le temps de mélange est relié à la capacité de pompage de l'agitateur. Le temps de mélange semble approximativement proportionnel au temps nécessaire à un seul cycle de circulation pour le liquide, ce temps étant étal au rapport du volume liquide à la capacité de pompage de l'agitateur.

L'auteur établit des lois générales pour choisir la meilleure forme et les meilleures dimensions des agitateurs à partir des relation dérivées pour le temps de mélange et la puissance consommée.

Il a fait quelques expériences dans le cas, à l'état stationnaire, du mélange de deux liquides alimentant en continu une capacité. Les résultats obtenus concordent avec ceux des expériences en discontinu.

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1. INTRODUCTION

1.1. *Definitions*

" Mixing " is understood to be any operation used to change a non-uniform system into a uniform one. A quantity of matter may be called *uniform* or *homogeneous* when the composition of a volume element of appropriate size does not deviate by more than a fixed amount from the average composition of the entire system.

Mixing is very often part of a chemical or physical process, such as blending, dissolving, emulsification, heat transfer, chemical reactions, etc. Chemical engineering recognizes it as one of the " unit operations " and it enjoys an increasing interest in literature. In spite of its importance mixing is still an " art " in most cases and the design of agitators and mixing vessels is largely based on experience [3] [6].

The devices for mixing are numerous ; they are greatly dependent on the purpose in view (e.g. heat transfer) and on the nature of the substances to be mixed (state of phase, consistency). As to the latter point, the state of phase greatly influences the choice of mixing method. Mixing can be classified according to the various combinations between the phases gas, liquid, and solid. Liquid-liquid mixing, for instance, is understood to be the mixing of two miscible or immiscible liquids. Important methods of mixing are : flow mixing, e.g. circulation by pumping, injection ; vibrational mixing, e.g. by ultrasonics ; mixing by rotating agitators [10].

In mixing two phenomena can be distinguished a splitting up of the volume elements and an interchange of these. In several cases, e.g. in mixing miscible liquids, the molecular diffusion also contributes to the ultimate homogeneity of the system to be mixed. In practice, the exchange by molecular diffusion, is negligible as compared with the eddy diffusion, due to the turbulence in the agitated system ; it is only important when considering volume elements of molecular dimensions.

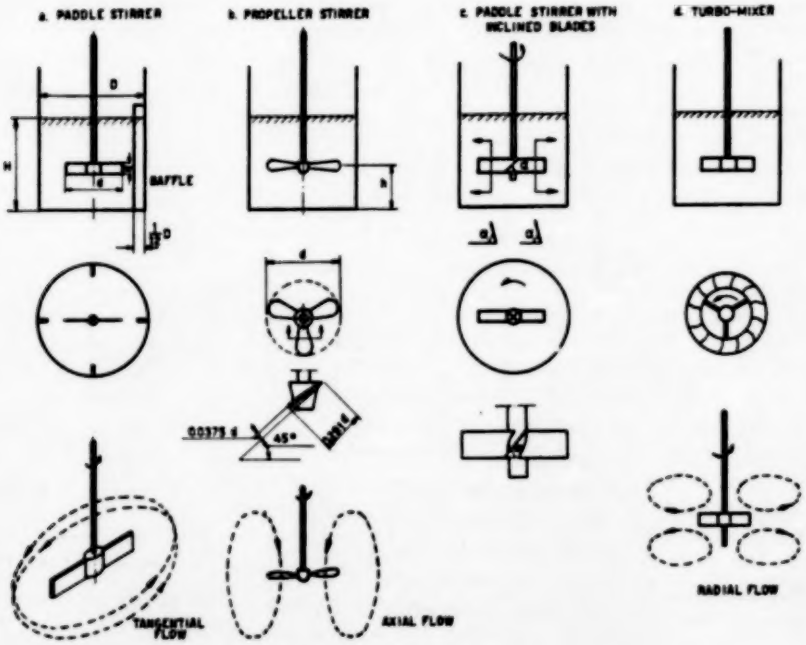

FIG. 1. Types of agitators.

1.2. *Various types of agitators and their flow pattern*

Mixing by agitation of liquids involves the transfer of momentum from the moving stirrers to the liquid. According to the way in which this occurs, stirrers may be divided into two categories :

(*a*) The momentum is transferred by *shearing stresses*, i.e. the transfer is perpendicular to the direction of flow. This category includes the cone stirrer, the bulb agitator, the rotating disc and others.

(*b*) The momentum is transferred by *normal stresses*, i.e. the transfer is in the direction of flow. This category includes the paddle stirrer, the turbomixer and the propeller (Fig. 1).

The latter three may in their turn be regarded as representatives of types distinguished according to flow pattern. We may distinguish three principal possibilities of flow according to the three axes of the coordinate system :

Tangential flow—This is found with all normal rotating stirrers, if no baffles or deflecting blades are present and the stirrer is placed centrally.

Axial flow—This is found with propeller type agitators.

Radial flow—This is found with turbine type stirrers (often fitted with deflecting blades), and to a certain extent with paddle stirrers.

As tangential flow does not contribute to the mixing in a vertical direction this type of flow is not particularly desirable. It will be shown later that tangential flow is always converted into radial flow by the centrifugal forces. This conversion can be promoted by baffling. In this way a " top-to-bottom " mixing is attained, as in the case of the axial and the radial flow pattern.

1.3. *Scope of the investigation*

The investigations on mixing are always based on a mixing criterion which permits an evaluation of the stirring process. As a rule, the choice of criteria depends on the systems to be mixed together with the purpose of the operation.

The present investigation is concerned with the mixing of miscible liquids. For this system the *mixing time* has proved to be an attractive criterion. *The mixing time is the time required to produce a uniform mixture of two miscible liquids.* In addition to the mixing time, the power consumption of the stirrer under various stirring conditions is measured. By comparing the mixing times and power consumptions of the various agitators conclusions can be drawn as to their efficiencies.

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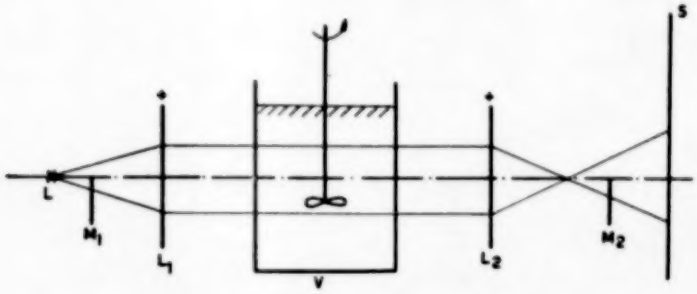

L = LIGHT SOURCE
L_1 = FIRST "SCHLIEREN" LENS
L_2 = SECOND "SCHLIEREN" LENS
V = MIXING VESSEL WITH STIRRER
S = SCREEN IN PLANE OF IMAGE OF V
M_1 = FIRST KNIFE-EDGE INTERCEPTING HALF OF THE BEAM
M_2 = SECOND KNIFE-EDGE (IN PLANE OF IMAGE OF M_1), INTERCEPTING THE OTHER HALF OF THE BEAM

FIG. 2. Experimental assembly.

2. Apparatus and Measuring Technique

2.1. *Mixing time*

The mixing time was determined by what is known as the " Schlieren " method. The arrangement, which is a modification of that used by TOEPLER [17], is represented schematically in Fig. 2. In order to avoid refraction the cylindrical mixing vessel was placed in a vessel with plane-parallel walls. Optical inhomogeneities in the liquid in the mixing vessel, in the form of gradients in refractive indices, will produce " Schlieren," whereas absence of the latter indicates homogeneity of the liquid mixture.

In these experiments we started from a condition in which the two liquids formed two superimposed layers. If the liquids are carefully introduced into the vessel the interface is clearly visible. The following liquids were used :

water and dilute solutions of acetic acid in water ;

water and dilute solutions of glycerol in water.

The mixing time was the time elapsing between the moment the stirrer starts mixing and the moment of disappearance of the " Schlieren." As to the reliability of the " Schlieren " method for this determination, the following may be noted.

It will be clear that the refractive index or the difference in refractive index has no influence on the time required to homogenize the two liquids. As stated above the " Schlieren " method is based on the fact that rays of light are deflected owing to refractive index gradients in the mixing vessel. It is therefore conceivable that the difference in refractive index influences the determination of the mixing time. Experiments have shown, however, that only the " intensity " of the " Schlieren " is influenced by this difference.

The mixing time as determined with this method proves to be independent of the difference in refractive index. Measurements made at a given difference in density give the same mixing time irrespective of the difference in refractive index. This phenomenon is in agreement with the observation that the intensity of the striae does not vary greatly during the mixing process until there is a sudden decrease at the end of the experiment (see figure).

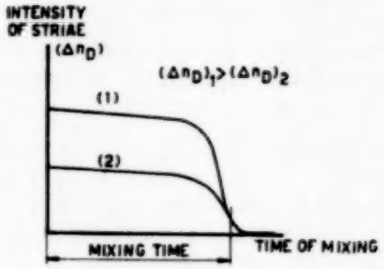

FIG. A

This behaviour can be explained by a study of the mechanism of the mixing process. It will be shown later that the mixing time is more or less equal to the time required to circulate the liquid once under turbulent conditions. During that time a continuous flow of liquid passes the stirrer, giving a striae image of fairly constant intensity. When all the liquid has passed the intensity decreases abruptly.

The moment of disappearance of the striae is dependent on the sensitivity of the method. However, if the moment immediately after the sudden decrease in intensity of striae (shown in the figure) is taken as the end point, the influence of the sensitivity is very small. It appears that the reproducibility is lower than 5% for various sensitivities of the set-up. The apparatus detected striae formation occurring at differences in refractive index of 10^{-5} under normal operating conditions. The difference in refractive index between the two starting liquids is of the order of 10^{-2}.

For laminar flow, the end point of mixing is very difficult to determine, as the transition to the homogeneous state is a gradual one. This is closely connected with the mechanism of the mixing process. Two effects play a rôle in reaching the uniform state : the long range convective mass transfer effected by the pumping action of the stirrer and the (eddy) diffusion between the small elements of volume.

In the case of turbulent flow the diffusion is so great that the mixing time is governed by the pumping action of the stirrer. With laminar flow

the diffusion is so small that the mixing time is controlled by the diffusion effect.

2.2. *Power consumption*

In the present investigation the following methods have been applied for the experimental determination of the power consumption :

(*a*) The stirrer is driven by a falling weight connected to the stirrer spindle by a piece of string. After release the weight first falls with an accelerated motion, subjecting the stirrer to a frictional torque in the liquid which increases with the speed and hence with the rate of fall. As soon as this frictional torque has become equal to the torque caused by the weight the motion will be uniform. The distance travelled by the weight per second multiplied by the weight gives the power consumption of the stirrer. Naturally, the experiment must first be carried out with the stirrer rotating in air to determine the frictional loss in the bearings, so that a correction can be made for this loss.

(*b*) The mixing vessel is placed on a rotary table. If the axes of stirrer and rotary table are parallel the couple required to prevent rotation of the vessel is equal to the couple exerted by the stirrer (the whole system is at rest and the resultant is therefore equal to zero). The angular velocity multiplied by the couple is equal to the power consumption of the stirrer. This determination must also be corrected for friction in the bearings and is only applied in the case of relatively great torques. For small torques the accuracy is not sufficient.

3. Mixing Performance of Paddle Stirrers, Propeller Stirrers and Turbomixers

3.1. *Mixing time*

3.1.1. *Dimensional considerations*

The mixing time (T) was determined as a function of a number of variables. It was found to depend on the following liquid properties :

μ = final viscosity of the mixed product
ρ = density of mixed product
$\Delta\rho$ = difference in density between the liquids to be mixed and on the stirring conditions :
n = number of revolutions of stirrer per unit time
d = diameter of stirrer
D = diameter of vessel
H = height of liquid in vessel.

Moreover, it must depend on g = acceleration of gravity.

Other factors which influence the mixing are location and mounting of the stirrer (eccentricity), the ratio by volume of the liquids to be mixed, the shape of the vessel (presence of baffles) and the shape of the stirrer.

Let us first consider the mixing time T as a function of (n, μ, ρ, $\Delta\rho$, d, D, H, g). Together with T these quantities can be combined to 9-3 = 6 dimensionless groups. For these groups we have taken :

(1) $\dfrac{Tnd^3}{V}$, where V = volume of the liquid ($V \sim D^2 H$)

(2) $\dfrac{\rho n d^2}{\mu}$ = Reynolds' number

(3) $\dfrac{n^2 d^2}{gH}$ = Froude number

(4) $\dfrac{\rho}{\Delta\rho}$

(5) $\dfrac{d}{D}$

(6) $\dfrac{H}{D}$

The above quantities have been adapted to the mechanism of mixing, so that they also have a physical significance. It has already been said that the mixing time is mainly determined by the pumping capacity Q of the stirrer. Accordingly, the mixing time is proportional to the time required to pump all the liquid round once : $T \sim \dfrac{V}{Q}$. Thus, $\tau = \dfrac{TQ}{V}$ represents the number of times the volume of liquid has to be pumped round. Dimensionally, the expression for the pumping capacity has the form $Q = nd^3$. However, it is obvious that in correlations use must

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be made of expressions for the theoretical pumping capacity §th which take into account, not only the diameter d of the stirrer, but also type, shape and other dimensions (see table, Pumping Capacity 3.2.4). The dimensionless mixing time τ is then given by $\frac{TQ\text{th}}{V}$.

In these expressions for the pumping capacity only stirrer dimensions are involved. During mixing, however, other factors also affect the actual pumping capacity. For example, the rotating stirrer has to overcome a certain counter-pressure, because liquid of lower density is pushed into liquid of higher density, thus reducing the pumping capacity. This influence is characterized by a density Froude number giving the ratio of the dynamic head of the flowing liquid, which is assumed to be proportional to $\rho n^2 d^2$, to the static head $\Delta\rho gH$ that has to be overcome. This quantity corresponds to the product of the

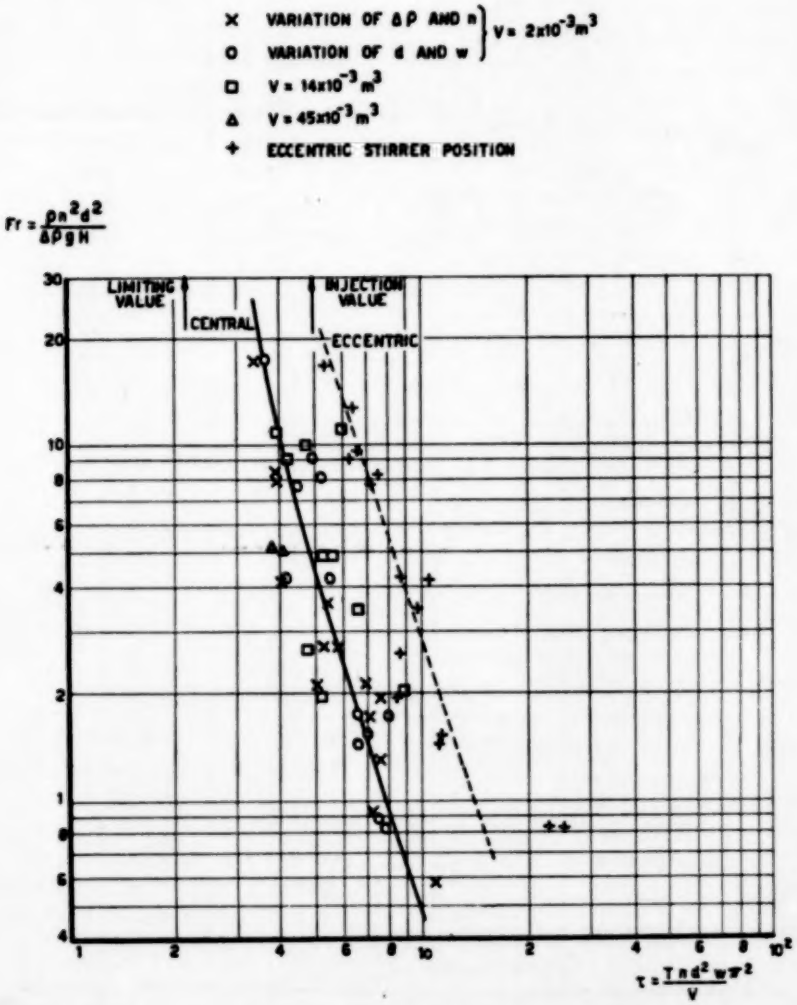

FIG. 8. Paddle stirrer with a right blade angle. Influence of the modified Froude number $\left(\frac{\rho n^2 d^2}{\Delta \rho gH}\right)$ on the dimensionless mixing time τ.

dimensionless groups mentioned in (3) and (4). With decreasing values for the quantity $\frac{\rho n^2 d^2}{\Delta \rho g H}$ the mixing time will naturally increase.

The dimensionless mixing time τ will also depend on the condition of flow in the mixing vessel, i.e. on Reynolds' number $\frac{\rho n d^2}{\mu}\left(=\frac{n d^2}{\nu}\right)$.

Finally, various length ratios play a rôle, notably those which give the dimensions of the stirrer in comparison with the total liquid volume. If the vessel is too large or of unsuitable dimensions in relation to the dimensions of the stirrer, "dead corners" with little turbulence will be formed, which lengthen the mixing time.

The expression for the mixing time may now

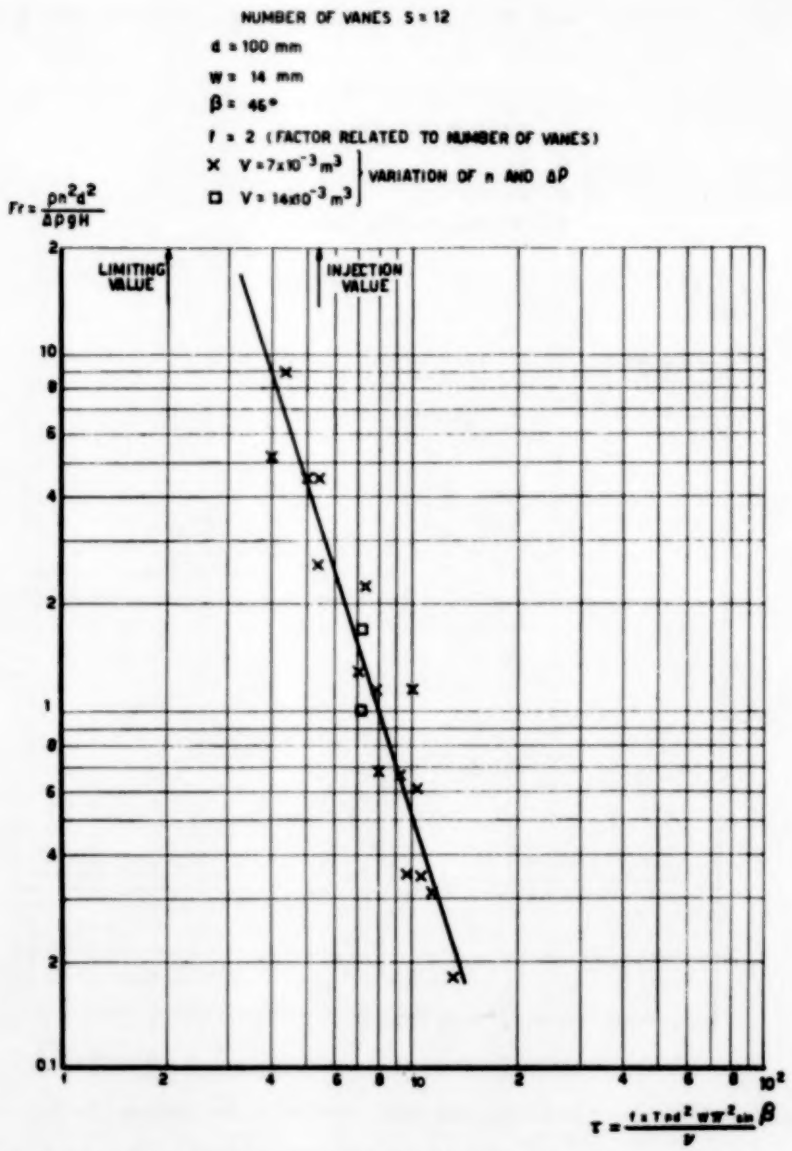
NUMBER OF VANES S = 12
d = 100 mm
W = 14 mm
β = 45°
f = 2 (FACTOR RELATED TO NUMBER OF VANES)
× V = 7x10⁻³ m³
□ V = 14x10⁻³ m³
VARIATION OF n AND Δp
Fr = ρn²d² / Δpg H
LIMITING VALUE
INJECTION VALUE
τ = f x 7πd² W² sin β / ν

FIG. 4. Turbomixer. Influence of the modified Froude number on the dimensionless mixing time.

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be formulated as $\tau = f\left(\frac{nd^2}{\nu}, \frac{\rho n^2 d^2}{\Delta \rho g H}, \frac{d}{D}, \frac{H}{D}\right)$.

During the correlation of the data we tried to represent the right-hand side of the equation by a product of functions, viz.

$$\tau = f_1\left(\frac{nd^2}{\nu}\right) f_2\left(\frac{\rho n^2 d^2}{\Delta \rho g H}\right) f_3\left(\frac{d^3}{D^{2.5} H^{0.5}}\right) \qquad (1)$$

It is obvious that this will not always be possible, although here good results were obtained.

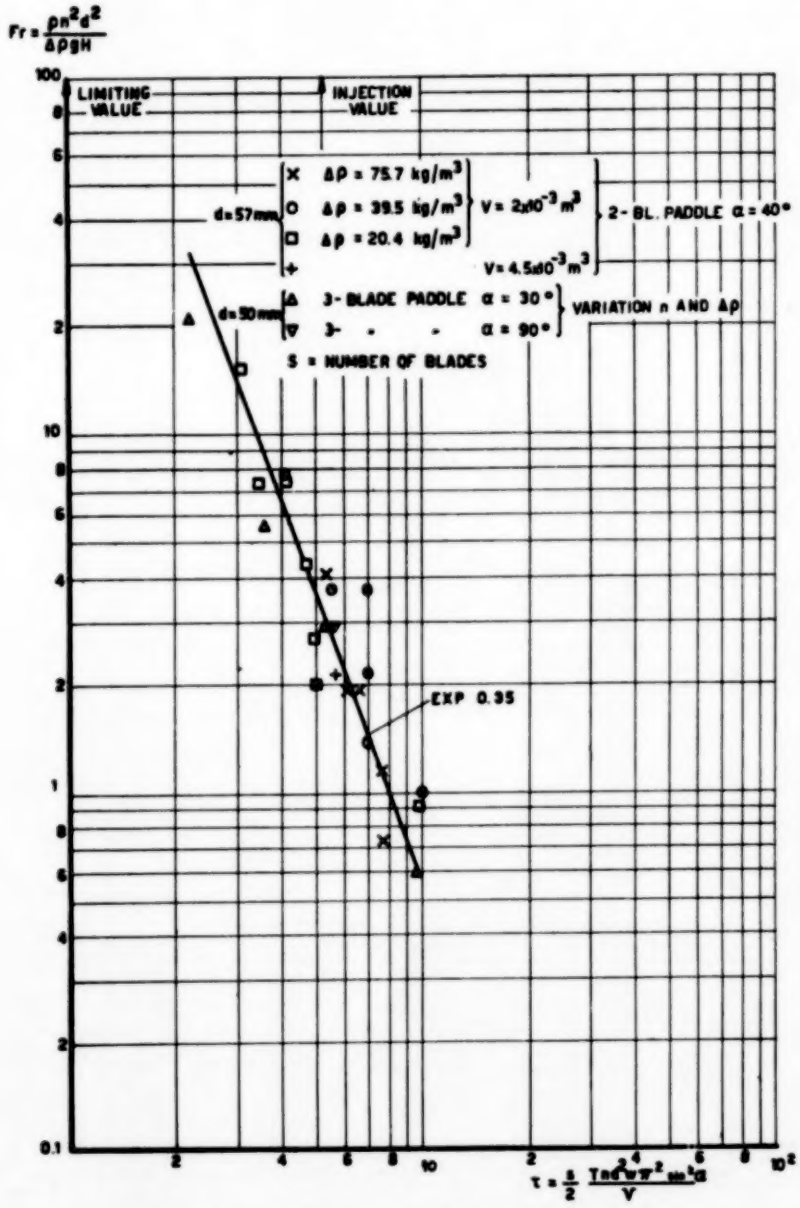

FIG. 5. Paddle stirrer with inclined blades.
Influence of the modified Froude number on the dimensionless mixing time.

3.1.2. *Influence of the density Froude number* $\frac{\rho n^2 d^2}{\Delta \rho g H}$ *on* τ

This relation is given for the various types of stirrer in Figs. 3, 4, 5 and 6.

The measurements on which the graph are based were carried out in a region where Reynolds' number and the length ratios have little influence. In a large region the relation may be represented by a power function :

$$\tau \sim \left(\frac{\rho n^2 d^2}{\Delta \rho g H}\right)^a \qquad (2)$$

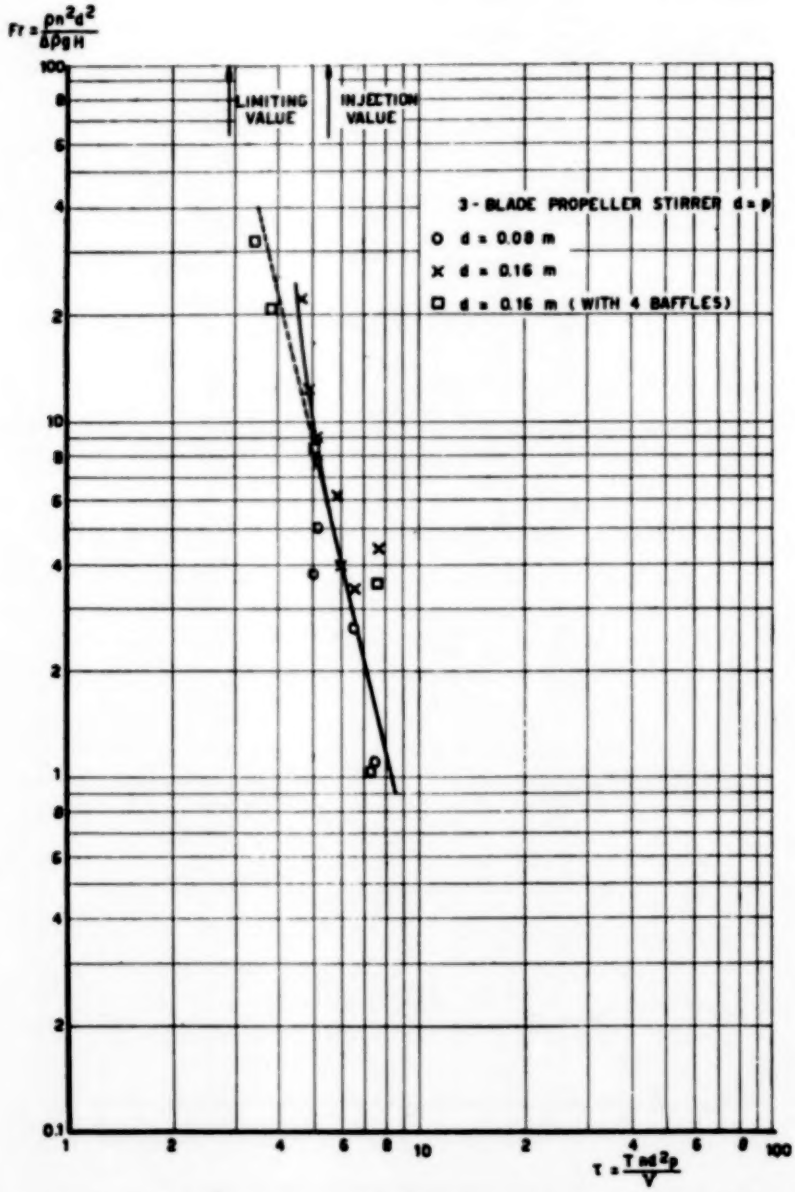

FIG. 6. Propeller stirrer. Influence of the modified Froude number on the dimensionless mixing time.

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where for a paddle stirrer $a = -0{\cdot}3$
a paddle stirrer with inclined blades $a = -0{\cdot}35$
a turbomixer $a = -0{\cdot}3$
a propeller stirrer $a = -0{\cdot}25$

For $\Delta\rho = 0$ the mixing time T approaches a finite positive value, which may be determined by extrapolation to $\Delta\rho = 0$ in a T vs. $\Delta\rho$ graph; hence, for very high $\frac{\rho n^2 d^2}{\Delta \rho g H}$ values τ approaches a limiting value.

We have also applied an injection method in some cases. Mixing-time measurements were carried out by suddenly adding a small amount of a glycerol-water mixture to the water during stirring, and measuring the time necessary for the striae to disappear. The results are indicated in

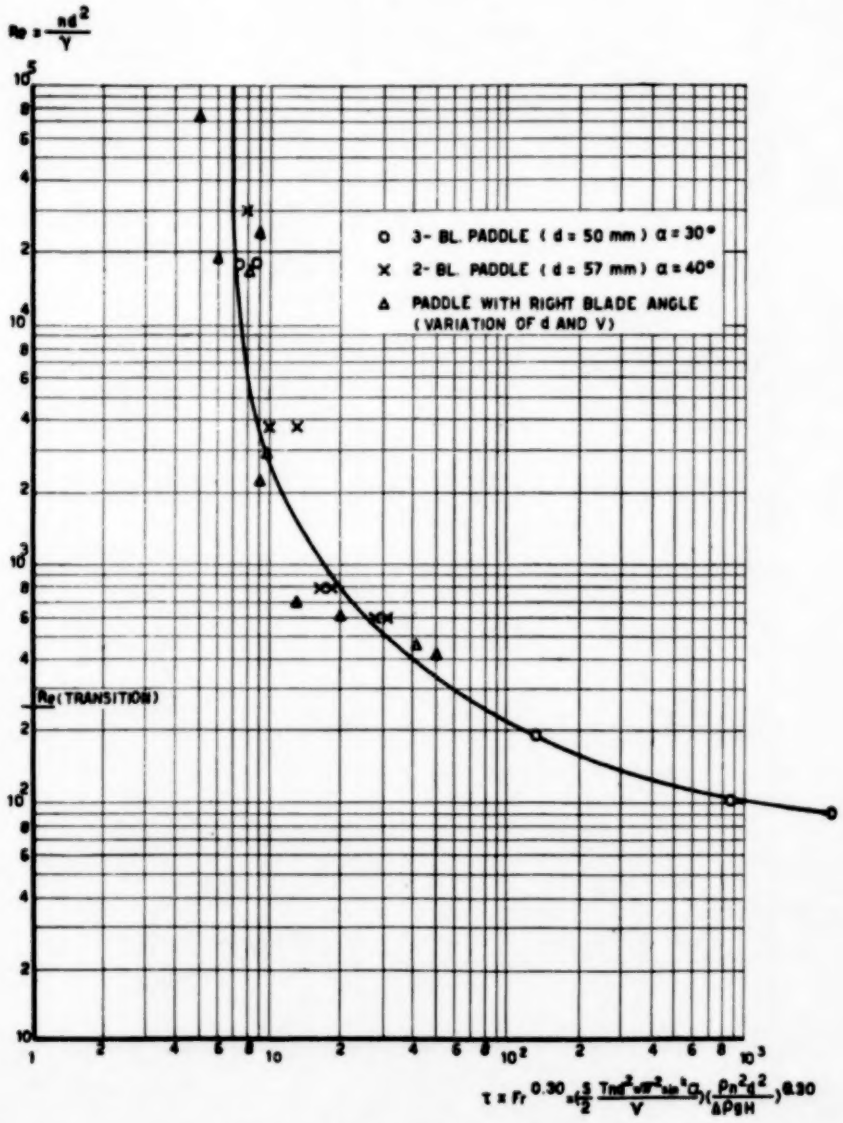
Re = nd²/ν
○ 3- BL. PADDLE (d = 50 mm) α = 30°
× 2- BL. PADDLE (d = 57 mm) α = 40°
△ PADDLE WITH RIGHT BLADE ANGLE (VARIATION OF d AND V)
Re (TRANSITION)
τ = Fr^0.30 sf^3/2 (Tnd²ωr²sin²α/V)(ρn²d²/ΔρgH)^0.30

FIG. 7. Paddle stirrer with right and with inclined blades. Influence of Reynolds number on mixing.

Figs. 3, 4, 5 and 6. The values found are invariably higher than the limiting values found by extrapolation to $\Delta\rho = 0$ in a T vs. $\Delta\rho$ graph, which suggests that in our experiments the quantity $\frac{\rho n^2 d^2}{\Delta \rho g H}$ still has some influence.

In addition, the influence of the volume ratio between the two liquids to be mixed was ascertained. As will be demonstrated in section 3.6, the increase in potential energy for a volume ratio of $\frac{\phi}{1-\phi}$ between the two liquids to be

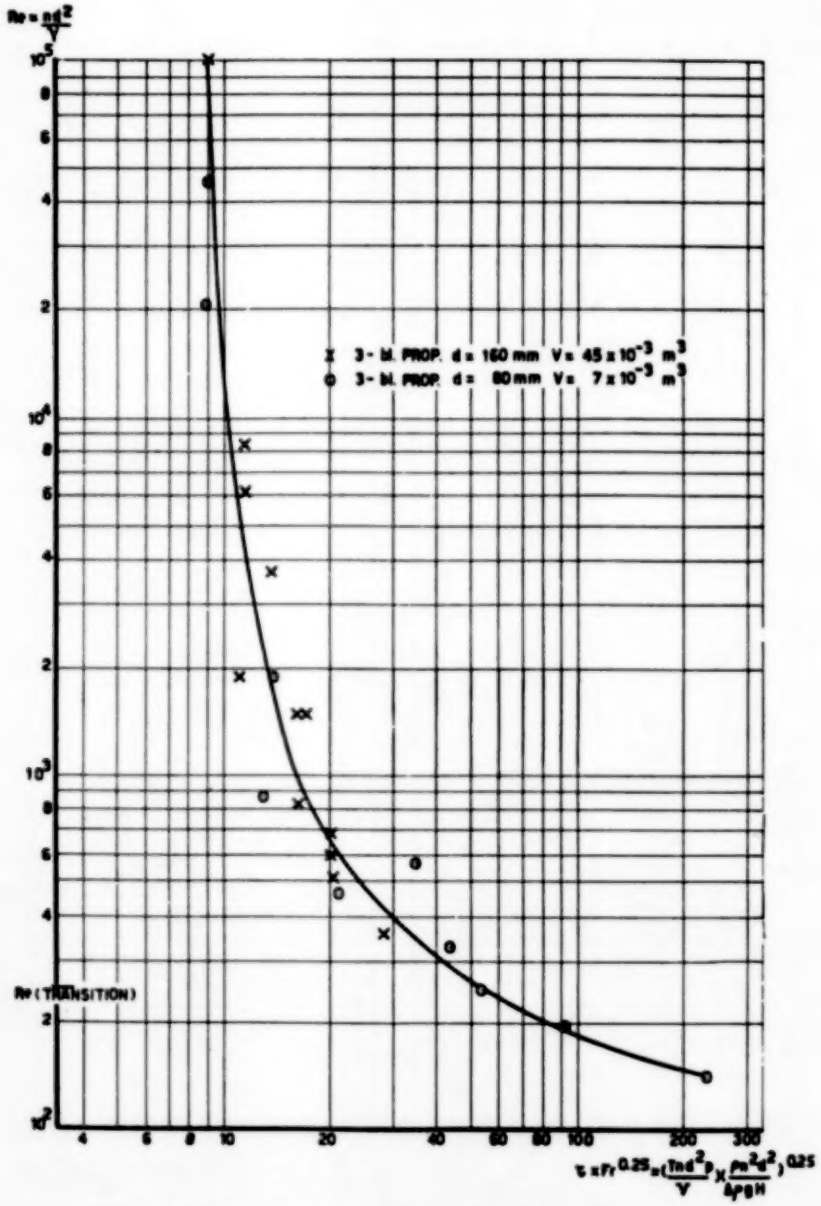

FIG. 8. Propeller stirrer. Influence of Reynolds number on mixing.

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mixed, at a constant total liquid volume, is equal to $\frac{1}{2}\phi(1-\phi)\Delta\rho g H V$. Now if for the density Froude number we take $\frac{\rho n^2 d^2}{4\phi(1-\phi)\Delta\rho g H}$ instead of $\frac{\rho n^2 d^2}{\Delta\rho g H}$ (which values are equal for the normal case of $\phi = 0{\cdot}5$), the results of the experiments with a varying ϕ can be correlated in the normal graph of dimensionless mixing time versus density Froude number.

3.1.3. *Influence of Reynolds' number* $\frac{\rho n d^2}{\mu}$

This relation is given in Figs. 7 and 8. For values $Re > 10^3$ to 10^4 the quantity $\tau \cdot \left(\frac{\rho n^2 d^2}{\Delta\rho g H}\right)^{-a}$ proved to be nearly constant.

For lower values it increases rapidly ($\tau \cdot Fr^{0.3} \sim Re^{-3}$). The type of flow is laminar, with persistent liquid eddies that show little exchange with their surroundings. Inhomogeneities are particularly persistent in the "dead corners."

The behaviour of the streamlines also revealed, for all stirrers studied, a transition from the laminar to the turbulent state. The streamlines could be made visible by introducing small gas bubbles into the rotating liquid. At a certain critical stirrer speed the track of the gas bubbles

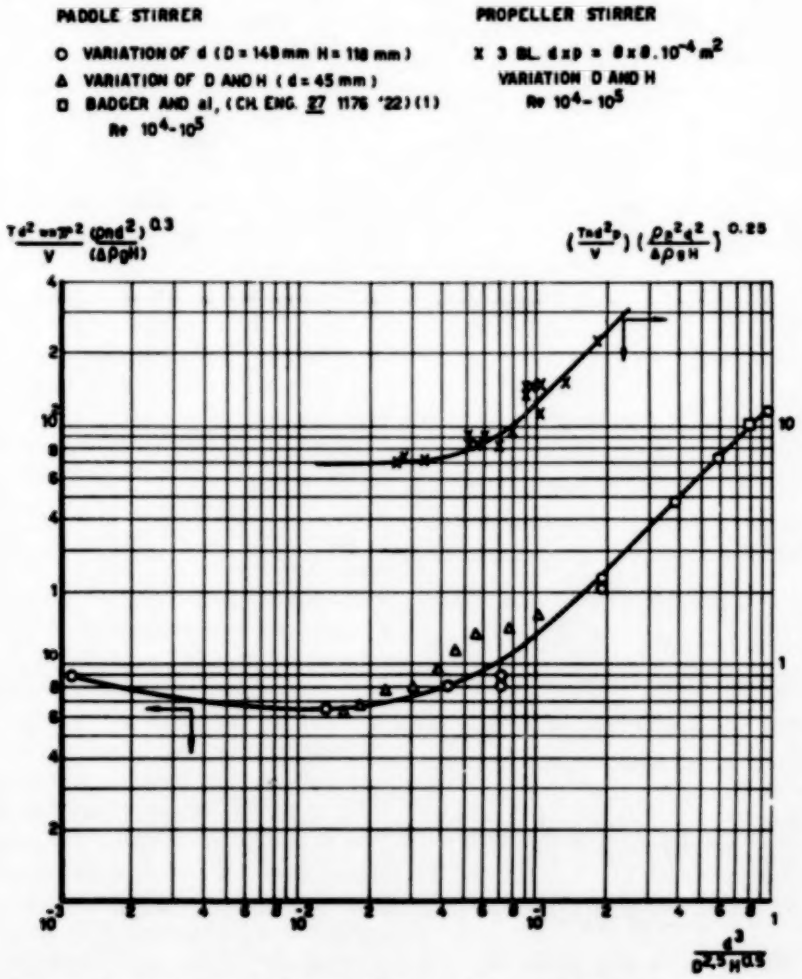
PADDLE STIRRER
○ VARIATION OF d (D = 148 mm H = 118 mm)
△ VARIATION OF D AND H (d = 45 mm)
□ BADGER AND al, (CH. ENG. 27 1176 '22) (1)
Re 10⁴-10⁵
PROPELLER STIRRER
X 3 BL. d x p = 8 x 8.10⁻⁴ m²
VARIATION D AND H
Re 10⁴-10⁵

FIG. 9. Paddle stirrer and propeller stirrer. Influence of the vessel dimensions on mixing.

becomes irregular. The change gradually set in at a value of the Reynolds' number : $Re_{transition} \cong 250$.

In the laminar region the mixing mechanism is no longer controlled by the pumping capacity but by the exchange between the more or less persistent liquid eddies. The concentration at a given point in the vessel approaches the equilibrium concentration much more gradually and there is no question of a sharp transition from not-yet-uniform to uniform composition of the liquid, as is the case in the turbulent range. In the laminar region sharp measurement of the mixing time from the striae image is not possible.

3.1.4. *Influence of dimensions of vessel relative to stirrer dimensions*

The relation is shown in Fig. 9. It was possible to include the $\frac{d}{D}$ and $\frac{H}{D}$ ratios in one combination, viz. $\frac{d^3}{D^{2.5} H^{0.5}}$. This quantity may also be written as $\left(\frac{H}{D}\right)^{0.5} \cdot \frac{d^3}{V}$ and more or less represents the ratio of stirrer volume to vessel volume. In the range $10^{-3} < \frac{d^3}{D^{2.5} H^{0.5}} < 4 \times 10^{-2}$ the quantity $\tau \cdot \left(\frac{\rho n^2 d^2}{\Delta \rho g H}\right)^{-a}$ is practically constant; outside this range it increases. For $\frac{d^3}{D^{2.5} H^{0.5}} < 10^{-3}$ the vessel volume is so large that dead corners are formed which lengthen the mixing time, whereas for $\frac{d^3}{D^{2.5} H^{0.5}} > 4 \times 10^{-2}$ the vessel volume is so small in relation to the stirrer volume that the movement of the liquid by the stirrer is impeded by the vessel wall being so near. For $\frac{d^3}{D^{2.5} H^{0.5}} > 10^{-1}$ the relation can be represented by a power function :

$$\tau \left(\frac{\rho n^2 d^2}{\Delta \rho g H}\right)^{-a} \sim \left(\frac{d^3}{D^{2.5} H^{0.5}}\right)^{+1}$$

3.1.5. *Influence of location of stirrer, etc.*

Eccentricity of stirrer—From the curves shown in Figs. 3-9 it is apparent that the behaviour of all types of stirrers is about the same. However, differences in the behaviour of stirrers occur when they are positioned eccentrically.

By eccentricity we understand the distance between the stirrer shaft and the axis of the mixing vessel divided by half the diameter of the vessel. The influence of the eccentricity on the mixing time is shown in Fig. 10. Unlike the influences discussed above, this influence proves to be greatly dependent on the type of stirrer. In the case of stirrers causing axial flow, like the propeller stirrer and the paddle stirrer with inclined blades, eccentricity shortens the mixing time. This is due to an increase in the relative velocity of the rotating stirrer and the liquid rotating with it. With an eccentric stirrer this relative velocity will be greater than when it is centrally placed. As will be shown in section 3.2.3 greater relative velocity causes a greater axial pumping capacity and therefore a shorter mixing time. In the case of stirrers causing tangential and radial flow, like the paddle stirrer (with straight blades) and the turbomixer, eccentricity lengthens mixing time. The tangential and radial pumping capacities also increase as the relative velocity increases. As, however, here the vicinity of the wall impedes the flow of liquid in a radial direction the mixing time becomes longer.

In the case of a paddle stirrer with the blades set at an angle α of 40° to 50°, the mixing time is found to be independent of the eccentricity, hence it may be assumed that here the two effects counterbalance each other.

Influence of the clearance between stirrer and bottom of the vessel—KRAMERS and KNOLL [8] have ascertained this influence for a propeller stirrer. Their measurements show that a clearance equal to half the liquid height generally ensures the shortest mixing time. Our own experiments with a paddle stirrer pointed in the same direction (Fig. 11). The investigation into the influence of this variable was therefore discontinued. Accordingly, in all experiments the clearance was equal to half the liquid height, unless stated otherwise.

Influence of inclination of the stirrer shaft—Rotation of the liquid with the stirrer can be suppressed, not only by an eccentric position of the

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stirrer, but also by placing the stirrer in the mixing vessel in an inclined position. When the stirrer shaft of a propeller is set at an angle of 30° or more to the axis of the mixing vessel the mixing time becomes about 0·7 times that under normal conditions. This effect, therefore is of the same magnitude as the influence of eccentricity of the stirrer.

Influence of baffles—In the experiments with baffles only the assembly shown in Fig. 1A has been studied. This type of baffles (mounted at right angles to the wall of the vessel) is commonly used in practice.

The object of placing baffles in the mixing vessel is to prevent the liquid from rotating with the stirrer. The ensuing advantage is that this counteracts vortex formation, which beats air into the liquid. Moreover, baffles cause the flow of liquid to be directed more axially, which generally has a favourable effect on the rate of mixing. In the case of propeller stirrers baffling has the same effect on the mixing time as eccentricity of the stirrer, especially at higher rotor speeds. The relative velocity of the stirrer and the liquid then approaches the stirrer speed, resulting in a higher pumping capacity. At lower

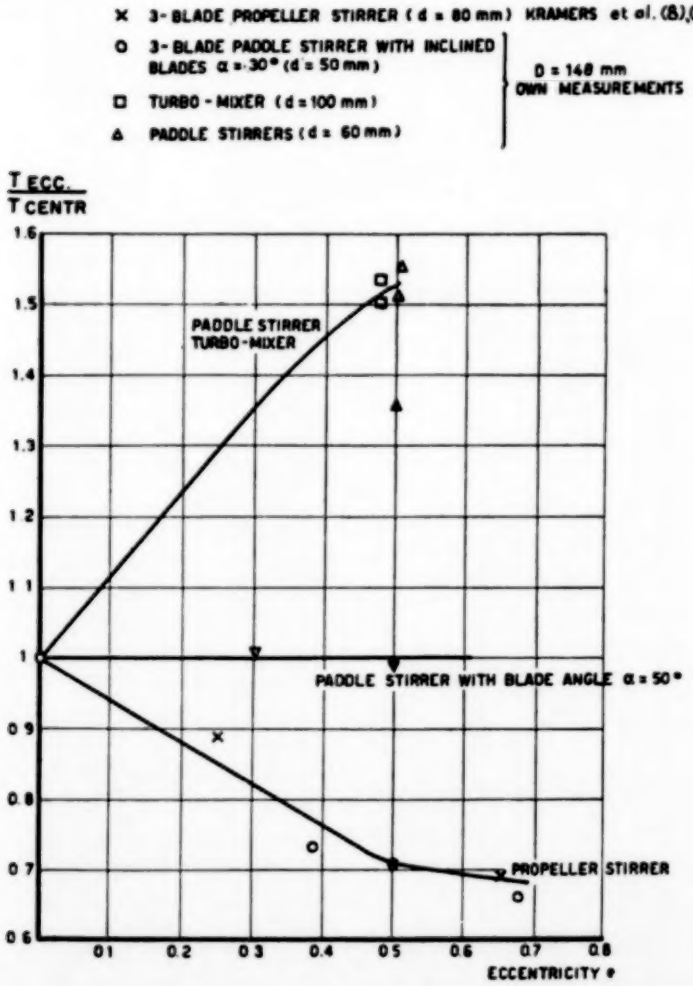

FIG. 10. Influence of eccentricity on mixing time

rotor speeds baffling has less influence on the flow pattern and on the mixing time.

With paddle stirrers and turbomixers baffling has about the same influence on the mixing time as with propeller stirrers. Turbomixers are often provided with deflecting stator blades, resulting in a perfectly radial flow pattern.

3.2. *Pumping capacity*

(influence of shape and dimensions of stirrer)

3.2.1. *Paddle stirrers and turbomixers*

When calculating the dimensionless mixing time $\tau = \frac{TQth}{V}$, the theoretical pumping capacity, Qth, must be expressed in characteristic and measurable quantities of the stirrer.

We will successively deal with the pumping capacities of the paddle stirrers (with straight blades), the turbomixer, the paddle stirrer with inclined blades and the propeller stirrer.

The paddle stirrer with blades set at right angles imparts to the liquid a momentum that gives it a tangentially rotating movement. From the point of view of mixing this movement is undesirable,

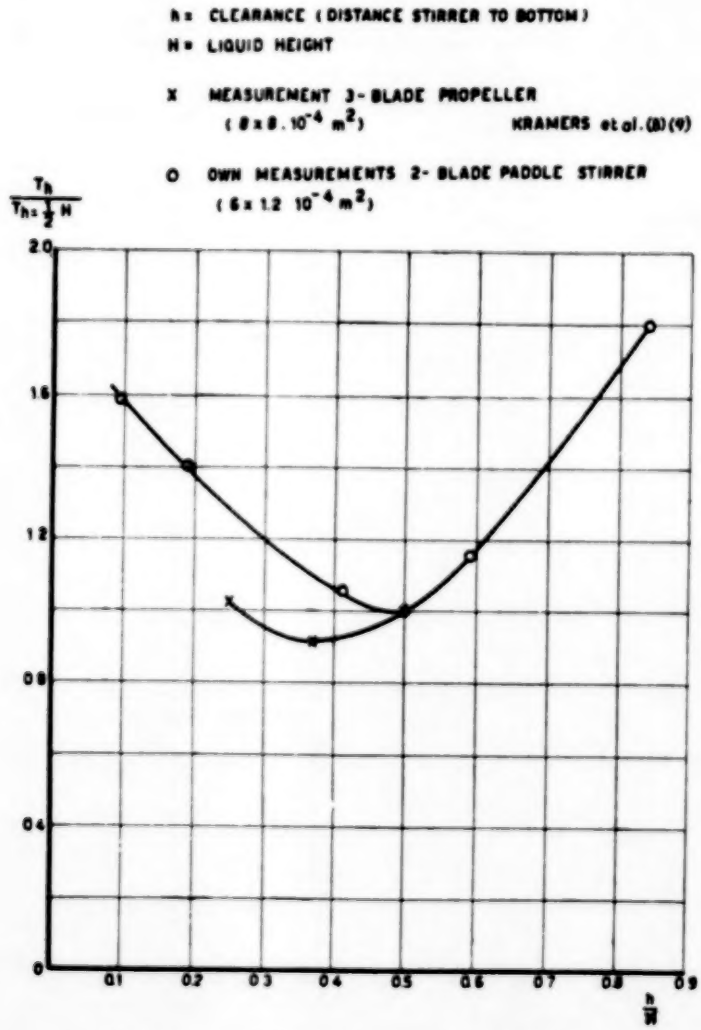

FIG. 11. Influence of clearance h on mixing time.

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because it does not contribute to mixing in a vertical direction, and hence cannot counteract the influence of gravity. The fact that the paddle stirrer nevertheless has a good mixing effect is due to a secondary radial flow pattern formed on account of the centrifugal forces set up.

The flow pattern of the turbomixer greatly resembles that of the paddle stirrer. Here, too, a radial flow is set up by centrifugal forces. Only the pumping capacity due to this radial flow has been considered. Since shape and action of the turbomixer are identical to those of the centrifugal pump the expression for the pumping capacity of a centrifugal pump can be used.

From the theory of centrifugal pumps it follows that the so-called " Euler's head " of the liquid leaving the centrifugal pump is equal to

$$h_E = \frac{c_2\, \omega r_2 \cos \alpha_2}{g}$$

where c_2 = absolute discharge velocity of the liquid from the vane,

α_2 = the angle that c_2 forms with the tangent to the circle having a radius r_2,

r_2 = radius of vane wheel (see figure).

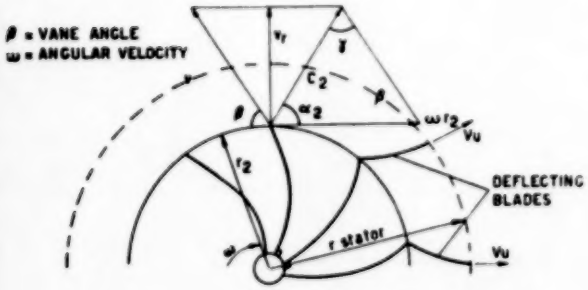

FIG. B. Discharge velocity diagram of turbomixer.

According to BERNOULLI's law : $h_E = h_{kin} + h_{stat}$ if friction losses in the pump are neglected.

When no deflecting blades are present $h_{kin} = \frac{1}{2} c_2^2/g$. The static head h_{stat} is assumed to be equal to the head $\frac{1}{2}(\omega_L/r_2)^2/g$, if ω_L = the angular velocity of the rotating liquid in the vessel.

Hence, $\rho c_2\, \omega r_2 \cos \alpha_2 = \frac{1}{2} \rho c_2^2 + \frac{1}{2} \rho (\omega_L r_2)^2$.

If $\frac{\omega_L}{\omega} = q\ (q < 1)$, it follows that $v_{rad} = c_2 \sin \alpha_2 = w r_2 \sin \beta \sqrt{1 - q^2}$, where β stands for the vane angle between the blades and the tangent to the circle having a radius r_2. When $q = 0$, $\alpha_2 = \gamma$ and $c_2 \sin \alpha_2 = \omega r_2 \sin \beta$.

The radial pumping capacity is the product of the annular area $2\pi r_2 w$ and v_{rad}

where w = width of stirrer blade ;

therefore the radial pumping capacity $Q = 4\pi^2\, n\, r_2^2\, w \sin \beta \sqrt{1 - q^2} = \pi^2\, nd^2\, w \sin \beta \sqrt{1 - q^2}$. For a paddle stirrer $\beta = 90°$ and $\sin \beta = 1$, therefore $Q = \pi^2\, nd^2\, w \sqrt{1 - q^2}$.

If all the liquid in the vesesl is rotating at an angular velocity ω, $q = 1$ and $Q = 0$.

If baffles are present $q = 0$ and $Q = \pi^2\, d^2\, wn \sin \beta$. The dimensionless mixing time $\tau = \frac{TQ\text{th}}{V}$ becomes $\tau = \frac{Tnd^2\, w\pi^2 \sin \beta}{V}$ and in the case of paddle stirrers $\tau = \frac{Tnd^2\, w\pi^2}{V}$.

When deflecting blades are present (as is often the case with turbomixers), again $h_E = h_{kin} + h_{stat}$. If v_u is the discharge velocity of the liquid from the stator, $h_{kin} = \frac{1}{2} \rho v_u^2$. If no rotation of the liquid in the vessel occurs h_{stat} may be assumed to be zero, hence $\rho c_2\, \omega r_2 \cos \alpha_2 = \frac{1}{2} \rho v_u^2$. Now $v_u = k c_2 \sin \alpha$, if $k = \frac{r_2}{r_{stator}}$. The radial velocity $c_2 \sin \alpha$ now becomes $c_2 \sin \alpha = \frac{\omega r_2 (-1 + \sqrt{1 + 2k^2 \operatorname{tg}^2 \beta})}{k^2 \operatorname{tg} \beta}$. In many constructions $k \approx 0{\cdot}7$, so $k^2 \approx \frac{1}{2}$, which gives:

$$c_2 \sin \alpha \approx 2\, \omega r_2 \left(\frac{+ 1 - \cos \beta}{\sin \beta} \right).$$

Compared with the turbomixers without deflecting blades, the pumping capacity is now larger by a factor $\frac{2}{1 + \cos \beta}$. Theoretically, the pumping capacity would become infinitely large for $\beta = 180°$. In practice the velocities for $\beta > 90°$ become so high that friction losses become important. As $\frac{1}{2} \rho c_2^2 + (h_{stat})_{rotor} = \frac{1}{2} \rho v_u^2 + 0$ and $c^2 > v_u$, $(h_{stat})_{rotor} < 0$, which means that

liquid will flow into the slit between rotor and stator. Consequently, $(h_{stat})_{rotor}$ will increase, and v_u, and hence the pumping capacity will decrease.

A gradual transition from paddle stirrer to turbomixer (without deflecting blades) could be studied by curving the blades and investigating the influence of β.

Experiments in which the influence of the vane angle β of a two-bladed stirrer on the mixing time was determined (the vane blade being curved in an arc) revealed that including a factor $\sin\beta$ in the formula for the dimensionless mixing time also has experimental significance (Fig. 12). The linear relation between $\sin\beta$ and $\frac{1}{T}$ suggests linearity between $\sin\beta$ and Q. Extrapolation to $\sin\beta = 0$ produces a finite value for T, although the theoretical radial pumping capacity would then have to become zero. Apparently, there is still some flow which causes mixing.

The influence of the blade width w on τ was

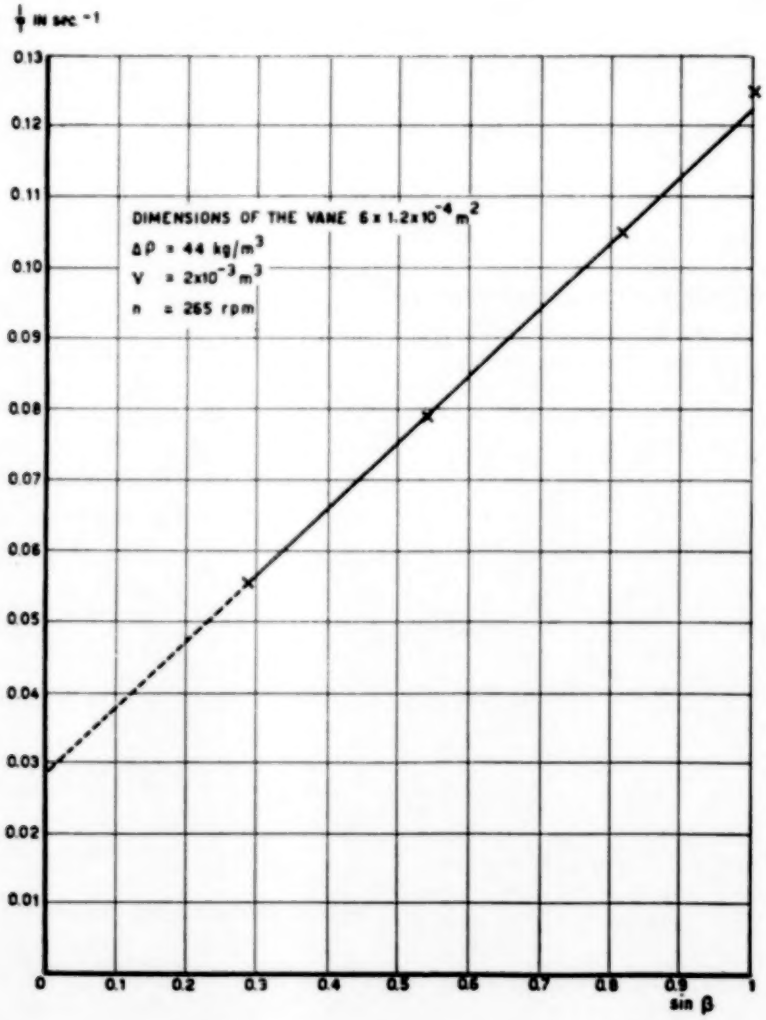

FIG. 12. Turbomixer 2 vanes. Influence of the curvature of the vane (vane angle β) on the mixing time.

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determined experimentally. It was found that Q is proportional to w for values of $\frac{w}{d}$ less than 0·5, which is in agreement with the above-mentioned expression $\tau = \frac{Td^2\, wn\pi^2}{V}$. For $\frac{\omega}{d}$ values of more than 0·5, τ increases with increasing $\frac{w}{d}$, i.e. Q is then less than proportional to w.

3.2.2. *Paddle stirrer with inclined blades*

A type of stirrer intermediate between the paddle stirrer and the propeller is the paddle stirrer with blades set at angles of less than 90°. This might also be called a propeller stirrer with a pitch decreasing towards the shaft. The relation between blade angle α and pitch p is given by :

$$\tan \alpha = \frac{p}{2\pi r},$$

where r is the distance from the stirrer shaft.

This type of stirrer produces both an axial and a radial flow pattern. Depending on the blade angle one flow pattern will predominate. Generally, both occur and there is thus an axial and a radial pumping capacity : Q_{ax} and Q_{rad}. The total pumping capacity $Q = Q_{ax} + Q_{rad}$. The mixing time T can be found from $\frac{1}{T} = \frac{1}{T_{ax}} + \frac{1}{T_{rad}}$ if T_{ax} is the mixing time when only axial flow occurs, and T_{rad} the mixing time when only radial flow occurs.

The influence of the blade angle α on the axial and radial (tangential) pumping capacity can be determined (theoretically) from the figure below.

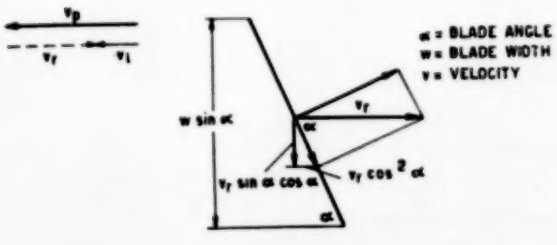

FIG. C.

Velocity diagram for a paddle stirrer with inclined blades.

The relative velocity v_r between paddle and liquid is equal to the paddle velocity v_p minus velocity v_l of the liquid rotating with the stirrer (assuming that v_l has no axial or radial component). Actually the liquid velocity v_l will form an angle with the paddle velocity v_p. The relative velocity $\boldsymbol{v}_r$ then becomes the vector difference $\boldsymbol{v}_l - \boldsymbol{v}_p$ and can be split up again into the components perpendicular to and parallel to the paddle blade. It is now assumed that the momentum of the component perpendicular to the paddle blade is destroyed. The result is then a velocity of the liquid relative to the paddle in the direction of the blade, which is equal to $v_r \cos \alpha$. The axial component becomes $v_r \cos \alpha \sin \alpha$ and the tangential component $v_r \cos^2 \alpha$. The absolute liquid velocity in tangential direction is then

$$v_p - v_r \cos^2 \alpha = v_r \sin^2 \alpha + v_l$$

The tangential velocity is reconverted into a radial velocity by centrifugal action.

Since the total liquid mass already has a tangential velocity v_l, the tangential speed relative to the surrounding liquid becomes equal to $v_r \sin^2 \alpha$ and the radial velocity, which is equal to the relative tangential speed, also becomes equal to $v_r \sin^2 \alpha$. The relative velocity v_r still depends on various factors. With an eccentric stirrer position and in the presence of baffles, v_r will increase and become approximately equal to the paddle velocity, resulting in an increased pumping capacity.

When the entire volume of liquid between the paddle blades has an axial velocity equal to $v_r \sin \alpha \cos \alpha$ and a radial velocity $v_r \sin^2 \alpha$ the axial pumping capacity becomes :

$$Q_{ax} = \int_0^{\frac{1}{2}d} \omega_r (\tfrac{1}{2}d) \sin \alpha \cos \alpha\, \pi\, d\, \partial\, (\tfrac{1}{2}d)$$

$$= \omega_r \sin \alpha \cos \alpha \frac{1}{12} \pi d^3$$

The radial pumping capacity becomes :

$$Q_{rad} = = \omega_r (\tfrac{1}{2}d) \sin^2 \alpha\, \pi d w \sin \alpha$$

$$= \tfrac{1}{2} \pi \omega_r \sin^3 \alpha\, d^2 w$$

For $\alpha = 90°$, $Q_{ax} = 0$ and $Q_{rad} = \pi^2 n_r d^2 w$.

Actually, it is not the entire volume of liquid $\frac{\pi}{4} d^2 w \sin\alpha$ that will have the above-mentioned velocity, but only a part γ of that volume, which may be represented by the sector with an angle of $\gamma \times 360°$. Then $Q_{ax} = \gamma \cdot \frac{1}{12} \pi \omega_r \sin\alpha \cos\alpha\, d^3$ and $Q_{rad} = \gamma \cdot \frac{1}{2} \pi \omega_r \sin^3\alpha\, d^2 w$. The factor γ will be influenced by the number of blades, and when this is small (1 to 3) it will be proportional to it. Now if we assume that the mixing time is inversely proportional to the total pumping capacity ($Q_{ax} + Q_{rad}$) and that the relative velocity v_r is proportional to the circumferential velocity of the paddle, T becomes

$$T \sim \left(\frac{1}{6} \pi^2 n \gamma d^3 \sin\alpha \cos\alpha + \pi^2 n \gamma d^2 w \sin^3\alpha\right)^{-1}$$

Experiments were carried out with a three-blade paddle, d being = 50 mm and w = 12 mm. The variation of T with α is then given by $T \sim (0{\cdot}7 \sin\alpha \cos\alpha + \sin^3\alpha)^{-1}$. Experimental testing of this formula shows that the relation is valid for $0° < \alpha < 60°$ (Fig. 13). In the range

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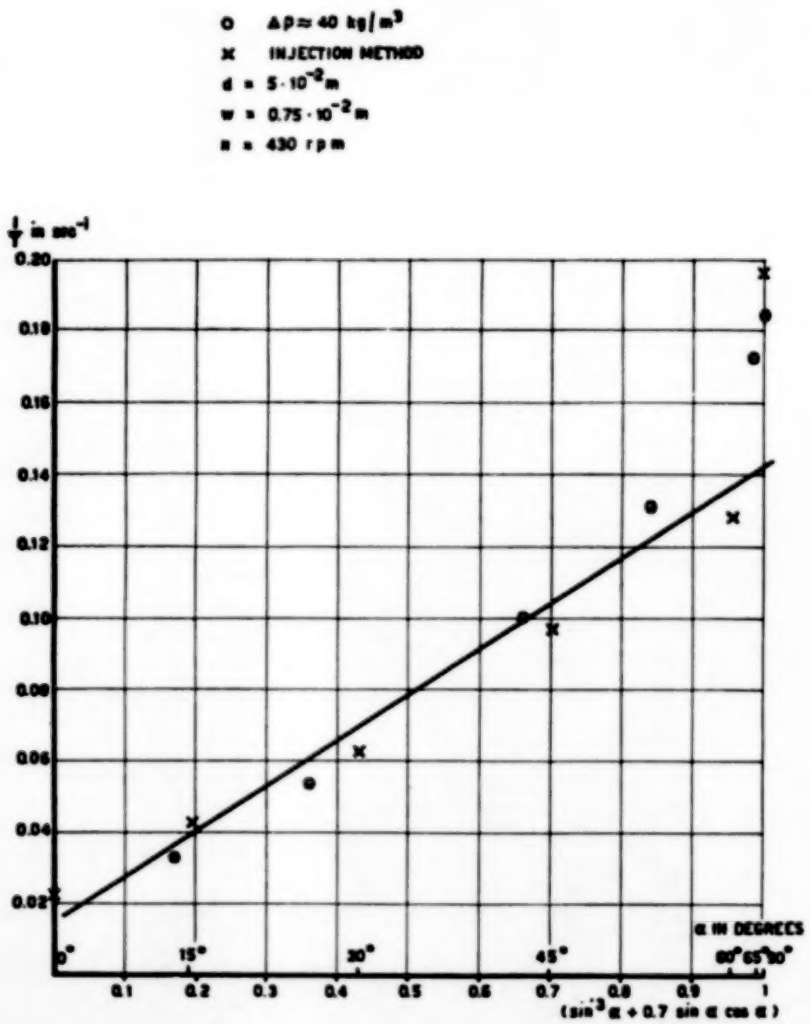

FIG. 13. 3-Blade paddle stirrer with inclined blades. Influence of the blade angle α on the mixing time T.

$60° < \alpha < 90°$ the experimental mixing time is shorter than that found with the aid of the above relation.

Correlation of the mixing time with sin α shows that for $40° < \alpha < 90°$ it is true that $T \sim \sin^{-2} \alpha$ (Fig. 14). For smaller angles $T \sim \sin^{-1} \alpha$.

The dimensionless mixing time τ used in the correlations was finally defined as follows for paddle stirrers with inclined blades :

$$\tau = \frac{Tnd^2w\,\pi^2 \sin^k \alpha}{V} \quad \text{(k being a function of } \alpha\text{)}$$

assigning to $\sin^k \alpha$ the value belonging to the angle α concerned ($1 \leqslant k \leqslant 2$).

In the case of paddle stirrers with a blade angle $\alpha = 90°$ the dimensionless mixing time is again reduced to the value already found, $\tau = \frac{Tnd^2w\pi^2}{V}$.

3.2.3. *Propeller stirrers*

The common propeller stirrer greatly resembles an ordinary ship's screw. It has screw-shaped blades with a constant pitch p. If the propeller is regarded as a paddle stirrer with blades set at an angle we may here again derive an expression for the pumping capacity in accordance with what was found in 3.2.2. But here the blade angle α is not constant : it varies in such a manner that $\tan \alpha = \frac{p}{2\pi r}$, r varying from zero (near the shaft) to $\frac{1}{2}d$ (extremity of stirrer blade). Now :

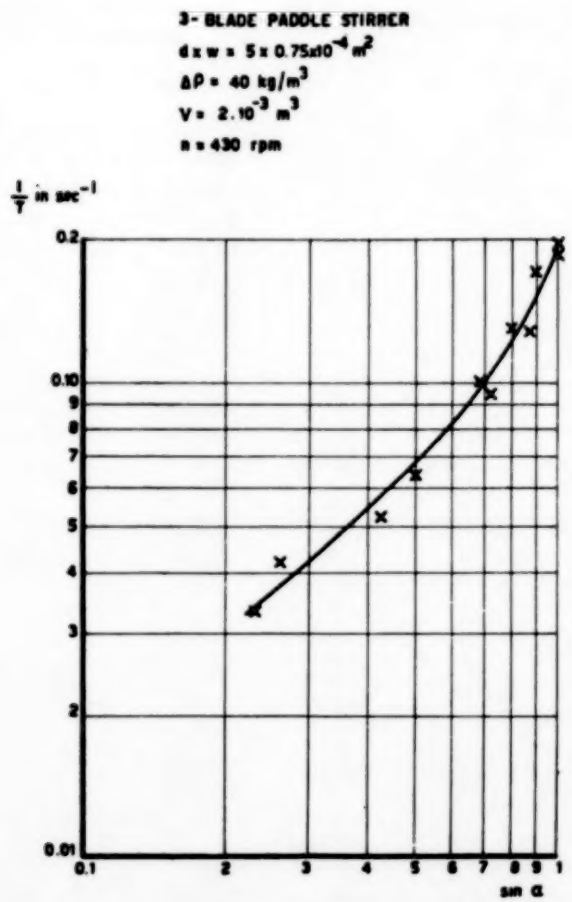

FIG. 14. Paddle stirrer with inclined blades. Influence of blade angle α on mixing time T.

$$\sin \alpha = \frac{p}{\sqrt{p^2 + 4\pi^2 r^2}}$$

$$\cos \alpha = \frac{2\pi r}{\sqrt{p^2 + 4\pi^2 r^2}}$$

The expression for the axial pumping capacity would become :

$$Q_{ax} = \int_0^{\frac{1}{2}d} 2\pi\omega \sin \alpha \cos \alpha \, r^2 \, \partial r$$

$$= 4\pi^2 \omega p \int_0^{\frac{1}{2}d} \frac{r^3 \partial r}{p^2 + 4\pi^2 r^2}$$

$$= \tfrac{1}{8} \omega a d^3 \left(1 - \frac{a^2}{\pi^2} \ln \left(1 + \frac{\pi^2}{a^2}\right)\right). \quad a = \frac{p}{d}$$

For the radial pumping capacity the expression for the radial velocity is found from :

$$\tfrac{1}{2} \rho v^2_{rad} = \int_0^r \rho\omega^2 \sin^2 \alpha \, r \partial r$$

$$= \tfrac{1}{2} \rho\omega^2 \frac{p^2}{4\pi^2} \ln \left(1 + \frac{\pi^2}{a^2}\right).$$

The radial pumping capacity then becomes $Q_{rad} = v_{rad} \pi d w \sin \alpha$

$$= \frac{\omega \, dpw}{2\sqrt{1 + \frac{\pi^2}{a^2}}} \sqrt{\ln \left(1 + \frac{\pi^2}{a^2}\right)}.$$

Hence, in spite of the rather simple flow picture on which the calculation is based the formula for the pumping capacity has already become fairly complicated. Therefore, these formulae are not suitable expressions in the dimensionless mixing time of a propeller stirrer. Considering that the flow picture of a propeller stirrer is mainly axial and that it follows from the equation for Q_{ax} that $Q_{ax} \approx npd^2$, the expression $\tau = \frac{Tnpd^2}{V}$ was chosen as the dimensionless mixing time. The pumping capacity of propeller stirrers was experimentally determined by RUSHTON and co-workers [14].They found that under optimum conditions the axial pumping capacity is directly proportional to the stirrer speed and to the square of the stirrer diameter. In later work they also found a proportionality between the axial pumping capacity and the pitch of the propeller [15].

These results give also experimental strength to the assumption that $Q \approx npd^2$.

3.2.4. *Recapitulation*

The expressions for the dimensionless mixing time in their relation to the stirrer type may be summarized as below.

The first three formulae (paddle stirrers and turbomixers) may be classified under one general formula :

$$\tau = \frac{Tnd^2 w \pi^2 \sin \beta \sin^k \alpha}{V}$$

which gives the mixing time for paddle stirrers (straight or inclined blades) as well as for turbomixers. This value of τ substituted in (2) gives a

Type of stirrer	*Flow pattern*	*Dimensionless mixing time* τ $\left(\tau = \frac{TQth}{V}\right)$	*Nomencleture*
Paddle ($\alpha = 90°$)	tangential	$\frac{Tnd^2 w \pi^2}{V}$	d = stirrer diameter w = width of blade β = vane angle α = blade angle p = pitch
Turbomixer (without deflecting blades)	radial	$\frac{Tnd^2 w \pi^2 \sin \beta}{V}$	
Paddle ($\alpha < 90°$)	tangential and axial	$\frac{Tnd^2 w \pi^2 \sin^k \alpha}{V}$	
Propeller	axial	$\frac{Tnd^2 p}{V}$	

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general formula for the mixing time, which is valid in the turbulent region for a vessel of appropriate size :

$\frac{Tnd^2 w\pi^2 \sin\beta \sin^k\alpha}{V}\left(\frac{\rho n^2 d^2}{\Delta\rho g h}\right)^{0.5} \approx 7$, whereas for propeller stirrers $\frac{Tnd^2 p}{V}\left(\frac{\rho n^2 d^2}{\Delta \rho g h}\right)^{0.25} \approx 9$.

Number of blades of the stirrer—Generally, paddle and propeller stirrers have either two or three blades. In the case of turbomixers the number of blades (vanes) is usually much larger (12-20). The influence of the number of blades on the pumping capacity was not extensively investigated. It was observed that experimental results correlate well when the pumping capacity is taken proportional to the number of blades, at least, when the latter is small (1, 2 or 3). When it is large, as for the turbomixer, this proportionality no longer holds true ; the pumping capacity then approaches a

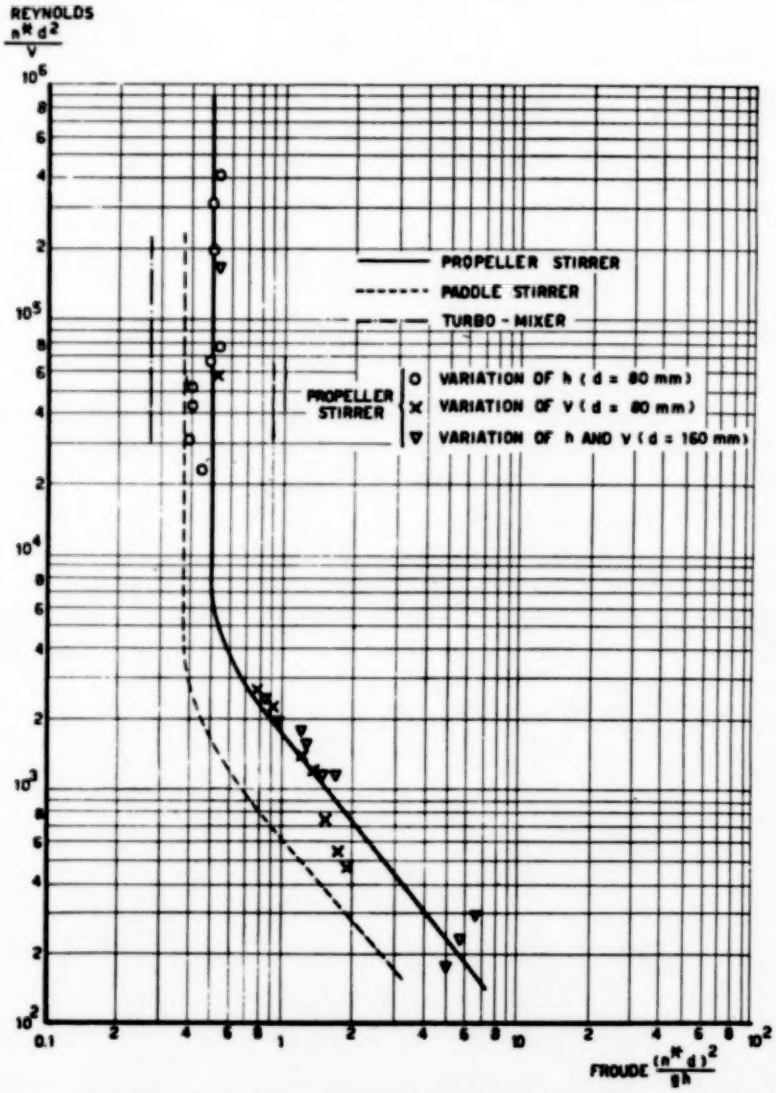
REYNOLDS
n* d²
ν
PROPELLER STIRRER
PADDLE STIRRER
TURBO - MIXER
PROPELLER STIRRER
VARIATION OF h (d = 80 mm)
VARIATION OF V (d = 80 mm)
VARIATION OF h AND V (d = 160 mm)
FROUDE (n* d)²/gh

FIG. 13. Vortex formation. Relation between Reynolds and Froude number at vortexing conditions.

maximum. The measurements with the turbo-mixer (12 vanes) may be made to coincide with the results obtained with the (two-blade) paddle stirrers if the pumping capacity is multipled by a factor 2 (f = 2).

3.3. *Vortex formation*

In most cases vortexing is undesirable because then gas is dispersed into the liquid. Moreover, mixing is not further improved when the speed of the stirrer n is increased beyond the critical speed n^* at which vortex formation starts. Results of measurements on vortexing caused by centrally placed stirrers could be fitted into a correlation between a dimensionless group of Froude, viz. $\frac{n^{*2}d}{g} \cdot \frac{d}{h} = \frac{n^{*2}d^2}{gh}$, and of Reynolds' number $\frac{\rho n^* d^2}{\mu}$ (Fig. 15) (h = distance between stirrer and level of liquid). For a Reynolds' number $> 10^4$ the quantity $\frac{n^{*2}d^2}{gh}$ proves to be constant. For low Reynolds' values ($Re > 10^3$) $\frac{n^{*2}d^2}{gh} \sim \left(\frac{\rho n^* d^2}{\mu}\right)^{0.8}$.

With the aid of these correlations the conditions to be used when vortexing must be avoided can be calculated in a very simple way.

3.4. *Rules for scaling up*

If a stirring apparatus is enlarged geometrically the conditions that have to be fulfilled to maintain the same mixing time in the large and small apparatus can be derived from (2).

For $Re > 10^3$-10^4, $\frac{Tnd^3}{D^3} \sim \left(\frac{\rho n^2 d^2}{\Delta \rho g H}\right)^{-0.3}$ (the exponent 0·3 being an average value) or $T \sim n^{-1.6} d^{-0.3}$, which means that $(nd^{0.2})$ must remain equal for T = constant. In practice this means that the number of revolutions of the stirrer should be nearly the same in the large and small apparatus. Generally, this claim will cause difficulties as the power consumption will then become too high. For $Re < 250$, $\frac{Tnd^3}{D^3} \sim \left(\frac{\rho n^2 d^2}{\Delta \rho g H}\right)^{-0.3} \left(\frac{\rho n d^2}{\mu}\right)^{-1}$ or $T \sim n^{-1.6} d^{-2.3}$, which means that $(nd^{1.4})$ must remain constant for T = constant.

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